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METALS and ALLOYS

The Magazine of Metallurgical Engineering

PRODUCTION • FABRICATION • TREATMENT • APPLICATION

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ARTICLES

The Spectrograph in the Iron Foundry 27
H. B. VINCENT, R. A. SAWYER AND A. M. SAMPSON

Effects of Controlled Atmospheres on Alloy and Carbon Steels—I 33
E. E. SLOWTER AND B. W. GONSER

High-Temperature Tests of Ni-Cr Alloys 40
KENNETH E. QUIER

The Hydride Process—II 45
PETER P. ALEXANDER

Lead-Calcium Alloys for Storage Batteries—An Extended Abstract 49
JANET Z. BRIGGS

Corrosion of Some Alloys by Ammonium Solutions ... 51
L. F. AUDRIETH AND T. E. FRANKS

Convention of the A.I.M.E. . . . . . A 5

Highlights . . . . . A 23

Editorial . . . . . A 25

Book Reviews . . . . . MA 121

Manufacturers' Literature . . . . . MA 123

Current News Items . . . . . MA 127

New Equipment and Materials . . . . . MA 130

METALLURGICAL ABSTRACTS

Ore Concentration . . . . . MA 80
Ore Reduction . . . . . MA 81
Melting, Refining and Casting . . . . . MA 82
Working . . . . . MA 86
Heat Treatment . . . . . MA 90
Furnaces, Refractories and Fuels . . . . . MA 94
Joining . . . . . MA 96
Finishing . . . . . MA 100
Testing . . . . . MA 102
Metallography . . . . . MA 104
Properties of Metals and Alloys . . . . . MA 110
Effects of Temperature on Metals and Alloys . . . . MA 114
Corrosion and Wear . . . . . MA 116
Applications of Metals and Alloys . . . . . MA 118
General . . . . . MA 119

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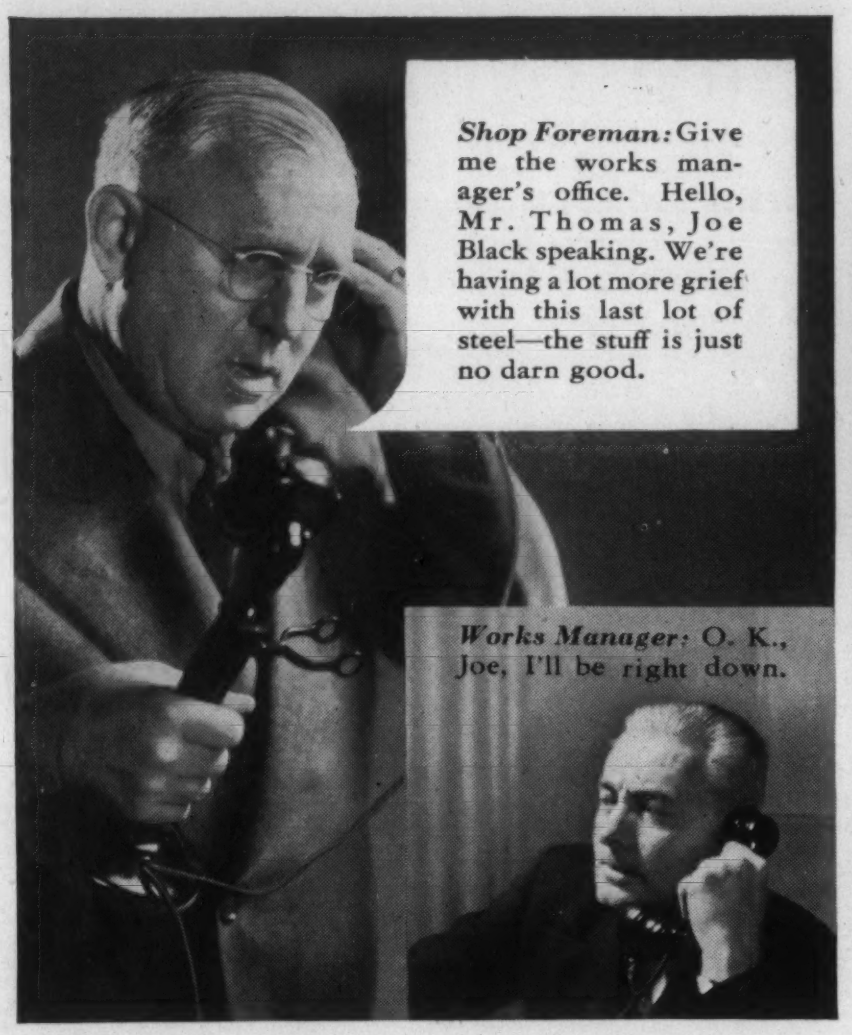
Shop Foreman: Give me the works manager's office. Hello, Mr. Thomas, Joe Black speaking. We're having a lot more grief with this last lot of steel—the stuff is just no darn good.
Works Manager: O. K., Joe, I'll be right down.

Works Manager: The Rockwell in this steel should run between 58 and 63 shouldn't it?
Shop Foreman: Yes, Mr. Thomas, but look what we're getting.
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UNITED STATES STEEL

The Spectrograph in the Iron Foundry

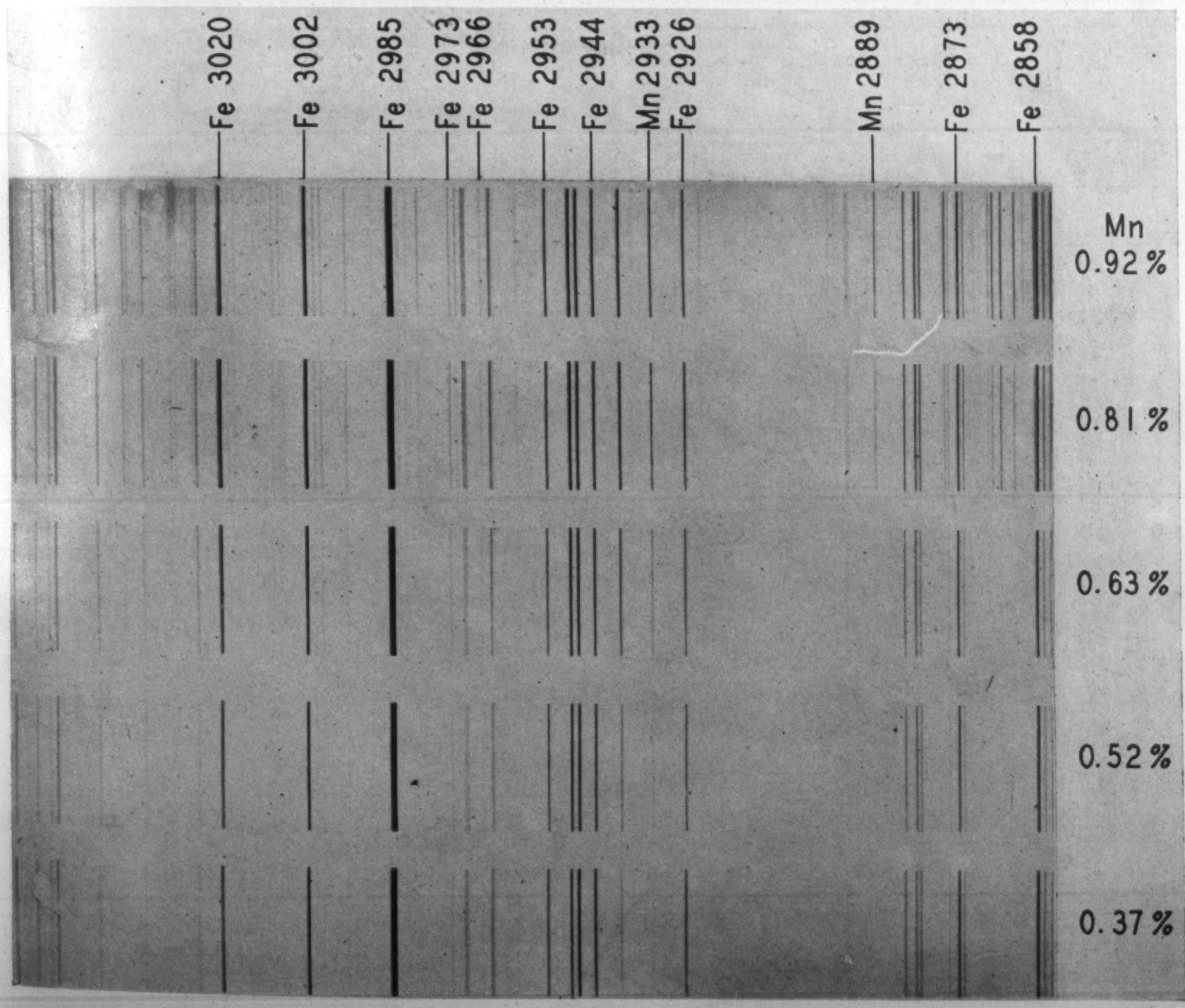
by H. B. Vincent, R. A. Sawyer and A. M. Sampson

Messrs. Vincent and Sawyer are in the Dept. of Physics, Univ. of Mich., and Mr. Sampson is with the Campbell, Wyant & Cannon Foundry Co.

The development described in this article was undertaken in 1934, through the department of engineering reseearch of the University of Michigan—a department devoted exclusively to cooperation with industries in technical developments,—the research being sponsored by the Campbell, Wyant and Cannon Foundry Company of Muskegon, Michigan, and carried out in the department of physics. It has been described by Vincent and Sawyer, Jour. App. Physics, *Vol. 8, 1937, pp. 163-173, and discussed by Oliver,* Iron Age, *Vol. 139, May 20, 1937, pp. 25-29. The present account is based on a verbal report at the Mass. Inst. Tech. Conference on Spectroscopy in July, 1937. This article describes a tripling of the speed of the process and an increase in its accuracy and range—a new stage in its development.—The Authors.*

FOR MANY INDUSTRIAL PROCESSES, the importance of rapid and accurate routine analysis can scarcely be overestimated, since it leads to diagnosis and cure of composition ills rather than postmortem lamentations. This fact has been generally recognized. For many years efforts have been made to increase analysis speed, not only by improving the wet methods of chemistry, but also by utilizing physical characteristics of the materials. Prominent among new developments has been

Fig. 1. Manganese in Iron. The blackening of the spectral lines of manganese increases with increasing concentration.



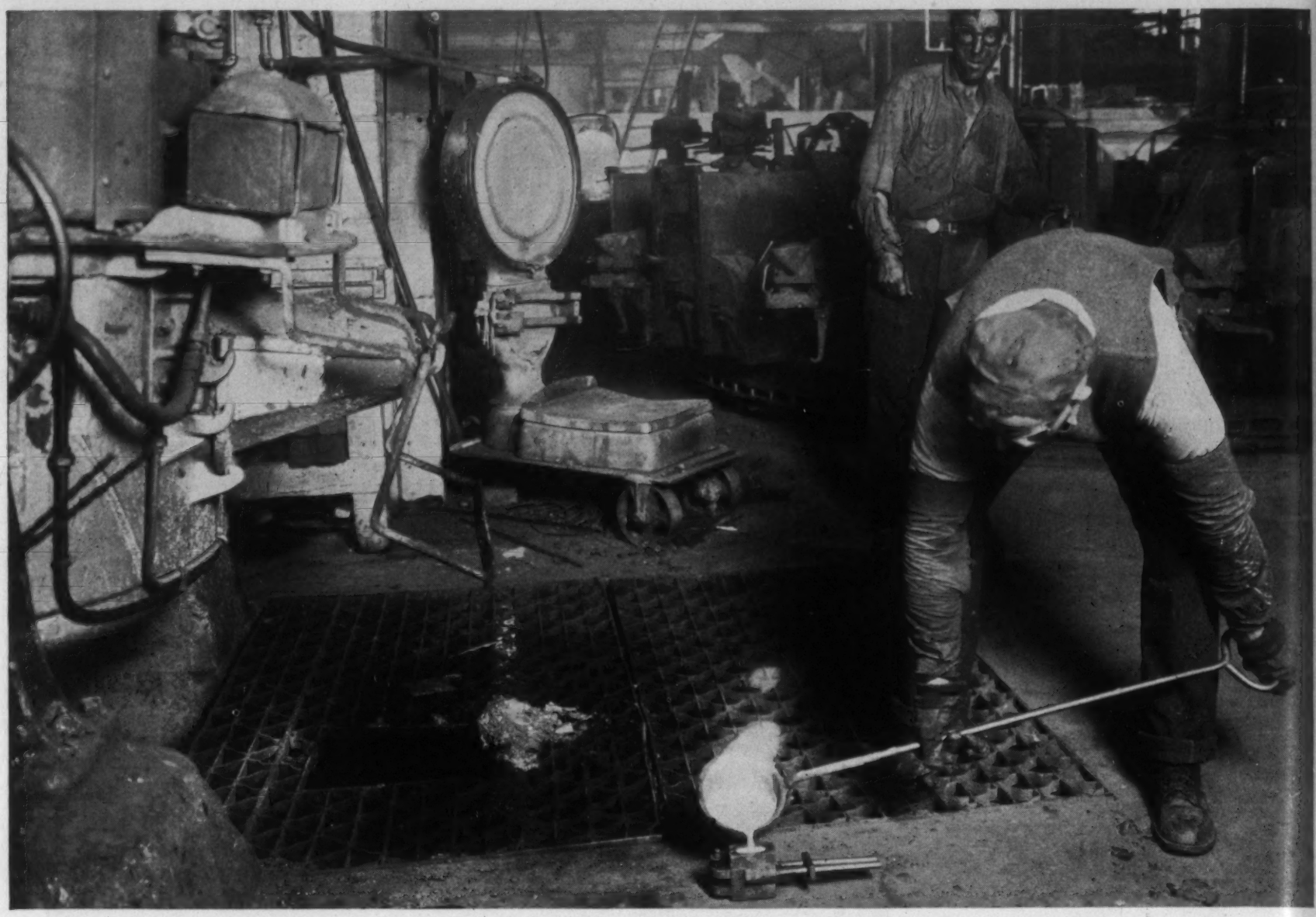


Fig. 2. Pouring Samples for Routine Spectrographic Analysis.

the use of the spectrograph. Its early successes were in qualitative analysis; quantitative results have until recently failed to attain the reliability demanded for industrial processes. However, satisfactory quantitative methods have been worked out in a number of instances and are in use by some of the more progressive industries.

Spectrographic Analysis of Cast Iron in 8 Mins.

During the past few years, the authors have developed, partly from suggestions contained in the literature and partly from their own investigations, a technique by which a sample of cast iron may be analyzed in 8 mins. elapsed time for the elements chromium, copper, manganese, molybdenum, nickel and silicon. In routine foundry use, the reliability of the analysis performed has been shown to be better than that of the chemical laboratory previously used; a production control and not simply an inspection analysis is provided.

An installation of apparatus, made at the plant of the Campbell, Wyant and Cannon Foundry Co., during 1935 and put in operation in the succeeding year, indicated that the spectrographic aspects of the problem had been solved. The analysis results showed adequate reliability and the elapsed time of 25 mins. needed for analysis of a single sample for 6 elements represented a considerable saving of time over gravimetric chemical methods. It was felt, however, that improvements in speed could be effected and, while the reliability of results was being tested by running duplicate samples in the spectrographic and chemical laboratories, the development of increased speed and some extensions of the analysis range were undertaken in the university laboratories.

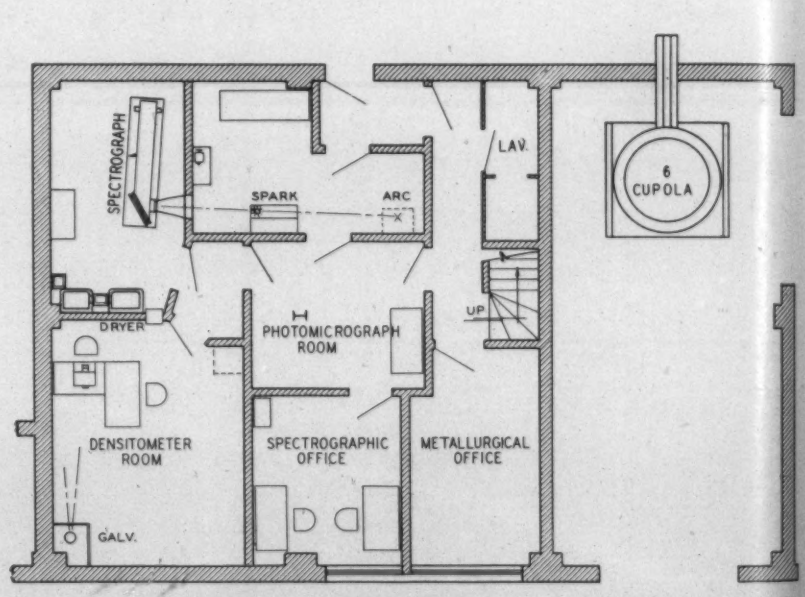
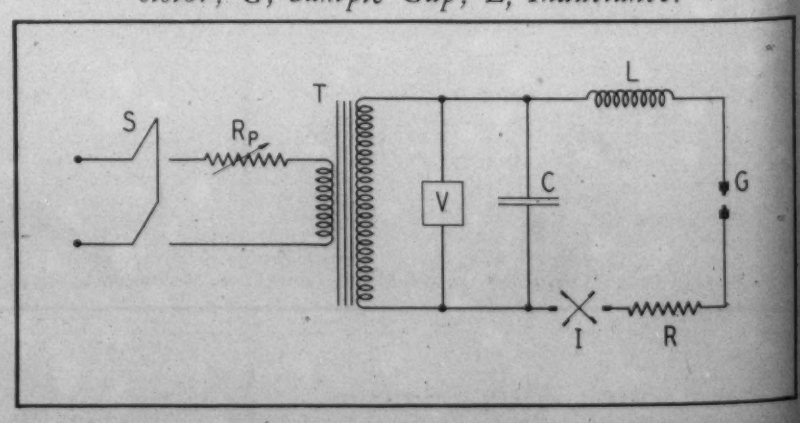


Fig. 3. The Spectrographic Laboratory. Note proximity to the line of furnaces whose output is analyzed.

Fig. 4. Circuit Diagram of Condensed-Spark Source, Comprising S, Line Switch; R_p Adjustable Primary Resistor; T High-Voltage Transformer; V, Electrostatic Voltmeter; C, Condenser; I, Synchronous Interrupter; R, Resistor; G, Sample Gap; L, Inductance.



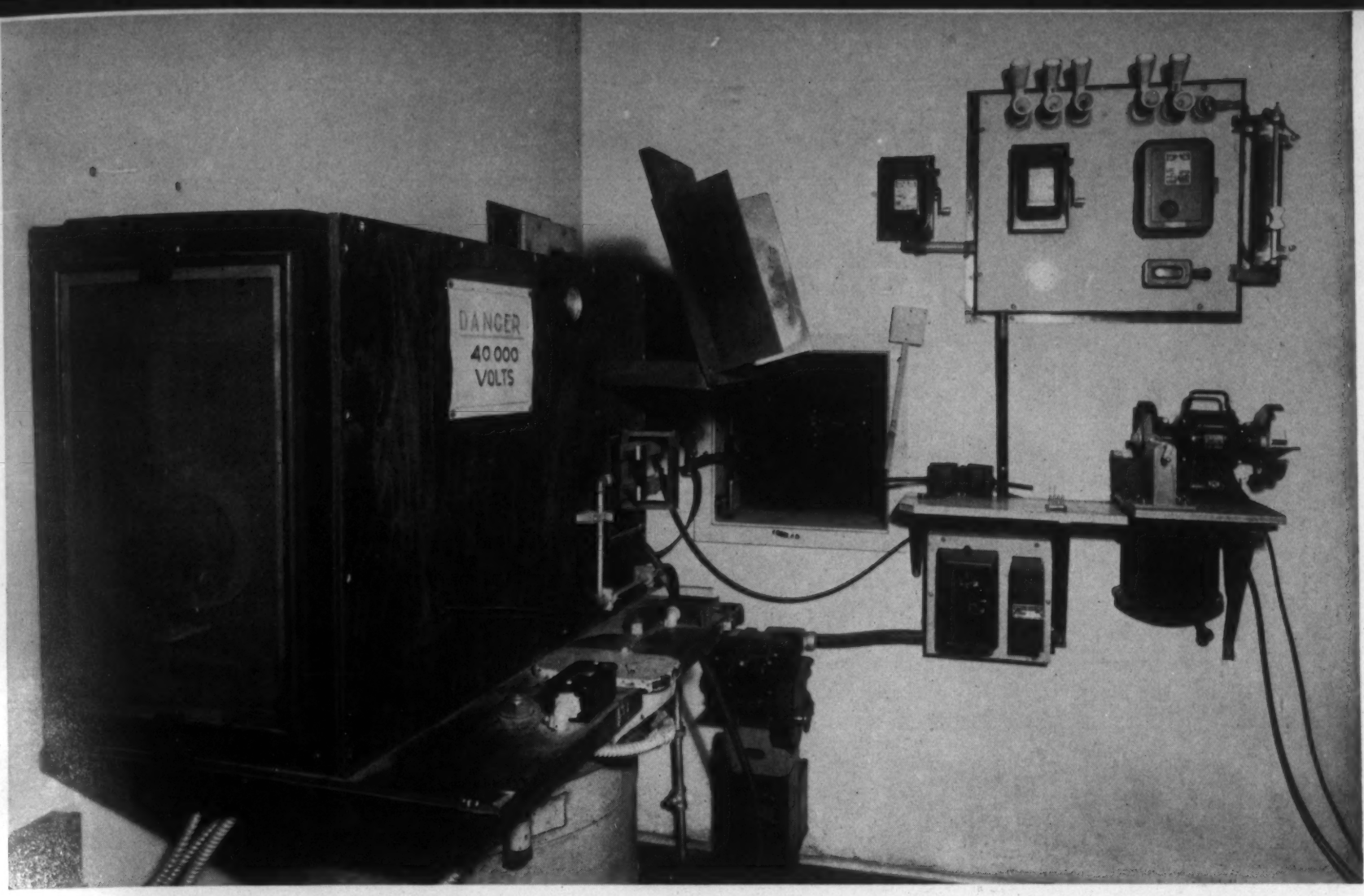


Fig. 5. The Source Room. The spark source operates from the power lines through a voltage regulator. The sample gap is protected by a cover operating a safety switch.

The ultimate results were the development of an 8-min. analysis technique, the demonstration of accuracy exceeding that of the chemical laboratory, and the taking over by the spectrographic laboratory of all routine control analysis for the metallic constituents of the irons. The company, which has long prided itself on the quality of its products, has found the rapid and accurate analysis of marked benefit in maintaining variation of composition within narrow limits.

Quantitative analysis by means of the spectrograph is based on the discovery, made many years ago, that if mixtures of metals containing various small concentrations of

Fig. 6. The Darkroom. The inclusion of the spectrograph in the darkroom saves many steps

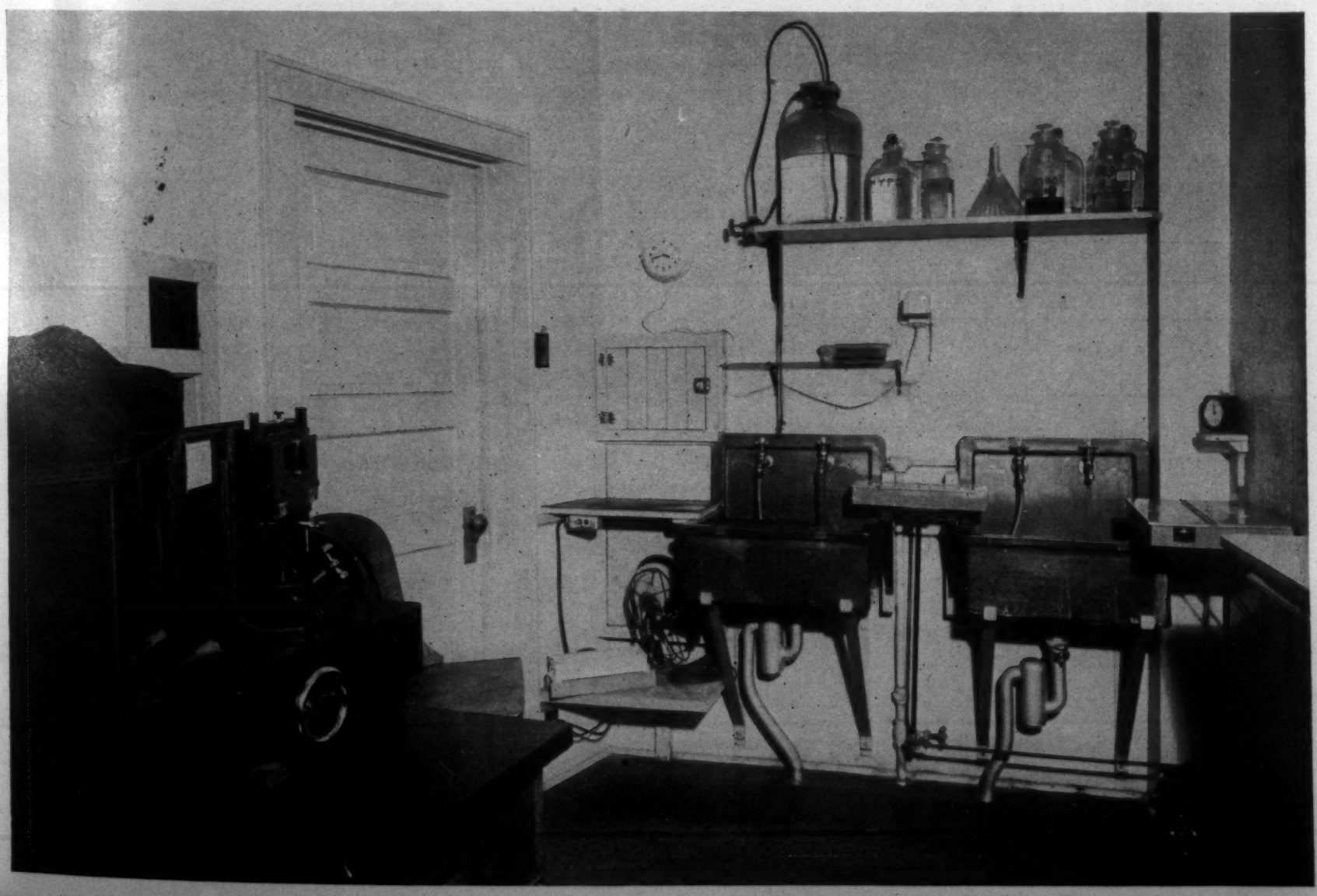


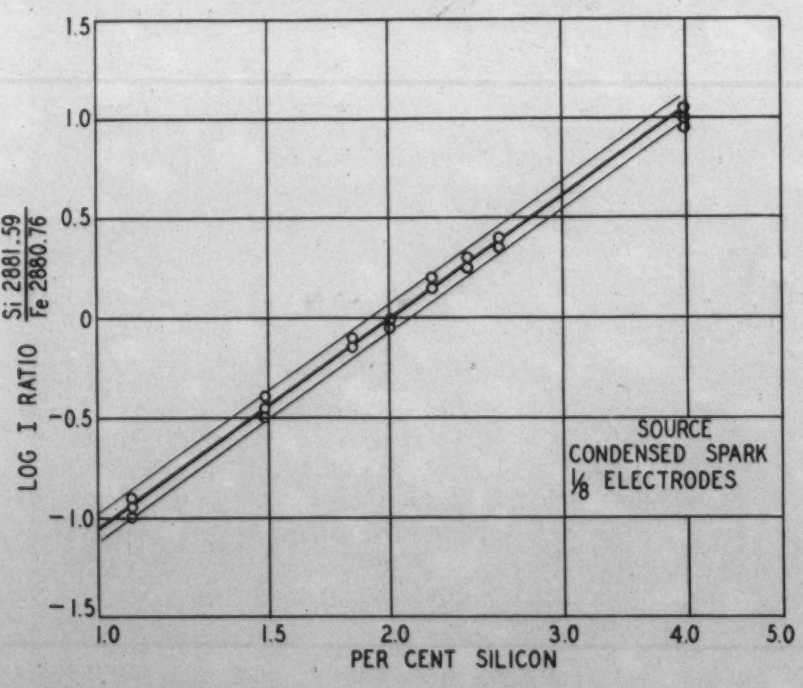
Fig. 7. The Microphotometer Equipment.

an element are used in a light source, such as an electric discharge, the spectrum due to that element varies in intensity with the concentration. An example of such variation, taken from the spectra of ferrous alloys, is given in Fig. 1.

How Calibration is Effected

In the process of quantitative analysis it has been found advantageous to base all calibrations on the relative intensities of selected element and matrix lines, since they are excited, exposed and developed together. Calibration is effected by establishing, by means of alloys of known composition, the relationship between relative intensity and percentage concentration. Such a plot is shown in Fig. 8. Samples, whose compositions are unknown, are analyzed by determining, from measurements, the relative intensities of the chosen pair of spectral lines, and reading the percentage content from the calibration curve. Continued use of standard samples is necessary only for occasional checks.

Fig. 8. Graph of Results Obtained with the Spark Source Shown in Fig. 4. Four readings are plotted for each sample. All readings in the working range fall within the outer lines which indicate ± 5 per cent of the amount present.



While, under a given set of excitation and exposure conditions, the range of percentage contents over which a spectral line shows satisfactory variation in intensity is quite limited, it has been found possible to choose lines and conditions such that the following percentages may be read simultaneously from a single spectrum:

Cr—0.01 to 1.50 per cent.
Cu—0.20 to 3.00 per cent.
Mn—0.30 to 1.25 per cent.
Mo—0.07 to 1.50 per cent.
Ni—0.15 to 2.00 per cent.
Si—0.50 to 4.00 per cent.

All irons in current production by the company fall within these ranges. Extensions are easily possible.

Analysis Procedure Described

In the analysis procedure at the foundry, cylindrical samples ⅛ in. in diameter and 1 in. long are poured from the molten iron into a permanent mold as shown in Fig. 2. They are immediately removed from the mold and taken to the spectrographic analysis laboratory. This laboratory,

shown in plan in Fig. 3, is provided with an independent air-conditioning system; the air is heated or cooled as desired, filtered, and maintained at a pressure slightly above atmospheric to prevent the infiltration of dust and smoke. The samples are burned in the spark source shown in Figs. 4 and 5.

The importance of the nature of the source used can scarcely be overemphasized. Indeed, the variation of spectral line intensity with concentration has long been known, and, beyond doubt, the spectrograph would be widely used for analytical work if it were not for the difficulty experienced in devising a discharge mechanism which will vaporize and excite an alloy in a repeatable fashion. The condensed-spark apparatus developed by the authors and constructed in the university instrument shops has proved entirely satisfactory for routine analytical work. It is thought to represent an advance over previous designs in stability and in the reproducibility of results.

The light from the spark source enters the spectrograph shown in Fig. 6. The installation of the spectrograph in the darkroom saves the maintenance and manipulation of dark slides, as well as much time and fatigue of the operators. The spectrum is recorded on a photographic plate

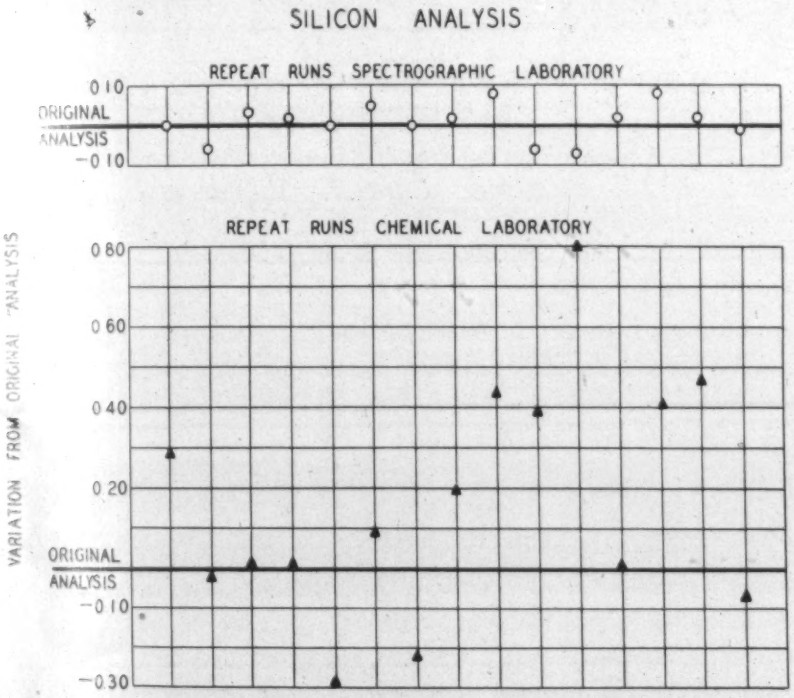


Fig. 9. Comparative Reliability. Production records at the foundry indicate that the spectrographic analysis is more reliable than analysis performed in the chemical laboratory. The original analysis is the heavy line, repeat analyses, the points shown. The silicon content is in all cases about 2 per cent.

in slightly less than 1 min. On completion of the exposure, the photographic plate carrying the spectral line image is processed and dried. This operation is completed in 5 mins. elapsed time through a special processing technique developed by the authors with the cooperation of Dr. C. J. Staud of the Eastman Kodak Co., Rochester, N. Y., and of J. S. Mertle of the Cramer Dry Plate Co., St. Louis.

The contrast of the photographic plate and the opacity of the selected spectral lines are measured with a remodelled Bausch & Lomb density comparator, shown in Fig. 7, and the readings transcribed to percentage content at the chart desk at the left. The instrument permits the reading of five or six spectral lines per minute and analysis results are available without extensive delays.

Actual tests have shown that a sample can be analyzed in 8 mins. elapsed time, and that it is possible to place in

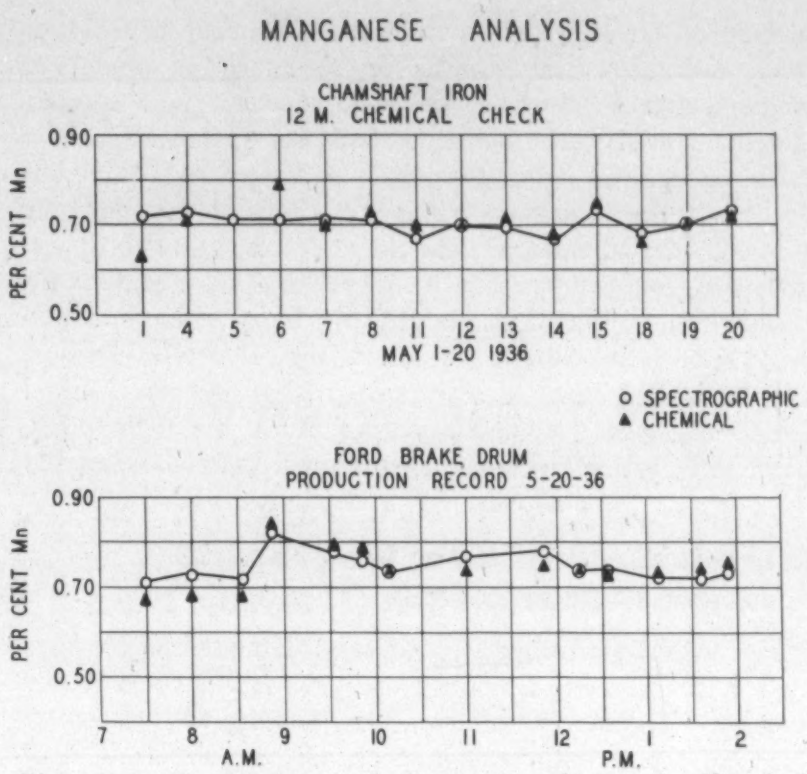


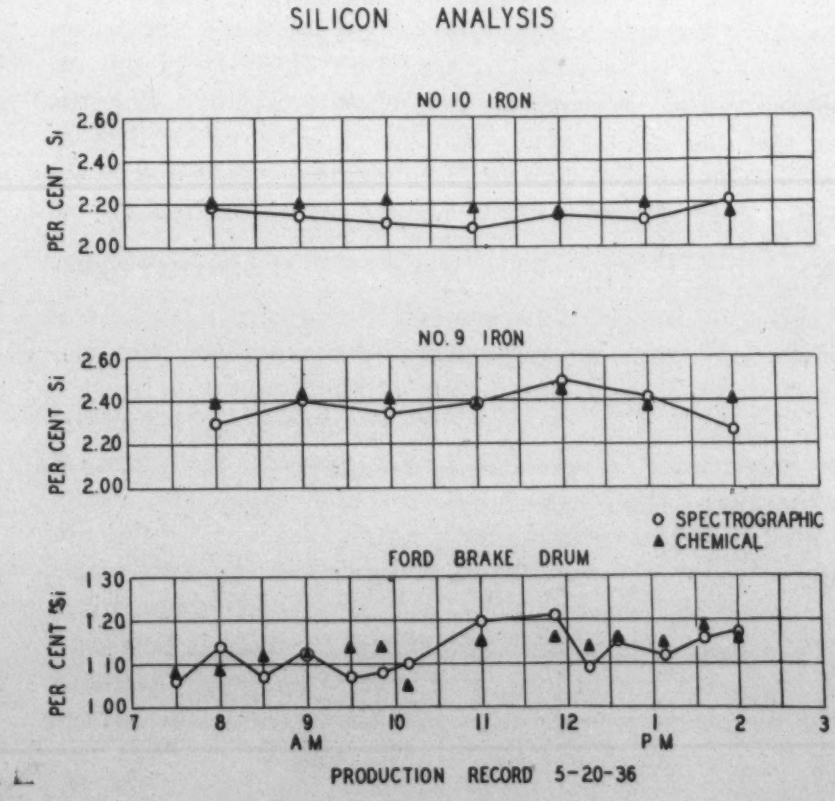
Fig. 10. Comparison of Spectrographic and Chemical Analyses for Manganese.

the hand of the furnace operator the analysis of a sample which he was pouring less than 9 mins. previously. Such analyses are carried out whenever casting difficulties are experienced with a particular melt, but, in normal procedure, samples are taken from all furnaces at regular half-hourly intervals and all analysis results are returned to the operators when the messenger makes his next trip for samples.

Precision as Important as Speed

Speed of analysis alone is not sufficient; precision is also of fundamental importance. If a method of analysis will not indicate very nearly the same composition when the sample is run a second time, it is useless for production control. The reliability demonstrated by the condensed-spark source is shown in Fig. 8, a graph of results obtained on samples analyzed chemically by expert analysts. An evaluation of results obtained in the foundry laboratory is

Fig. 11. Comparison of Spectrographic and Chemical Analyses for Silicon.



not based on any such careful chemical analyses. However, during several months of simultaneous operation, numerous check readings between chemical and spectrographic results were obtained. Samples to be analyzed in both laboratories were supposed to be poured from the furnace at the same time, but it is not possible to guarantee that the two laboratories had, in all cases, samples of exactly the same composition. Comparisons were made with routine-control chemical analysis which is, perhaps, somewhat more hurried than the best analytical determinations. In general, the press of arrival of new samples prohibited efforts to compose small differences in analysis. However, if the discrepancies were sufficiently great, one laboratory or the other might find time for a check run.

Chemical and Spectrographic Analyses Compared

Fig. 9 shows a comparison of original and repeat analyses for the chemical and spectrographic laboratories at the foundry. The readings shown here include, with no omissions, all the repeat runs made on silicon analysis in certain types of iron during the period March 1 to May 20, 1936. The original analyses lie on the heavy line and departures of the repeat analyses from the original are shown by the distribution of the points. The silicon content is, in all cases, about 2 per cent, and it is apparent that no repeat spectrographic determination differs from the original by more than 8 points, or 4 per cent of the silicon content, and that the limit of error from the mean does not exceed plus or minus 2 per cent of the amount of the element present. It is thought that a limit of error of plus or minus 5 per cent of the content is sufficiently liberal to include such systematic errors as may be anticipated. It is important to note that this is an unselected list of repeat analyses from an actual routine-control installation, that it covers an elapsed time of nearly three months and is not a quotation of results obtained on a single photographic plate in a development laboratory.

The repeat runs made in the chemical laboratory for the same element and the same irons over the same period show considerably wider departures. This graph does not, of course, represent the average chemical accuracy, since check readings were taken only in cases where the initial determination appeared questionable, either through failure to check the spectrographic result on the same sample, or because the composition appeared to differ from the expected value. Perhaps the best view to take of this figure is that the departures show the relative probability of something going wrong with the method. In any case, the spectrographic determinations show superior reliability.

Analyses for Mn and Si Compared

Figs. 10 and 11 show a comparison for manganese and silicon of routine spectrographic and chemical analyses performed on irons in production at the foundry. In general, analyses were made in the spectrographic laboratory at much more frequent intervals than in the chemical laboratory; the figures show all chemical results posted, and the corresponding values obtained by the use of the spectrograph. The period selected for comparison is random and covers a sufficient time to be representative.

The graphs show small differences in analysis but none of important proportions, and it must be borne in mind that the exact composition is not known, and that it cannot be guaranteed that the samples were of precisely the same composition. In view of Fig. 9, which demonstrates relative repeatability, perhaps no large part of the small variations observed should be assessed as errors in the spectrographed determinations. In any case, the accuracy of the spectrographic determinations is easily adequate for routine control.

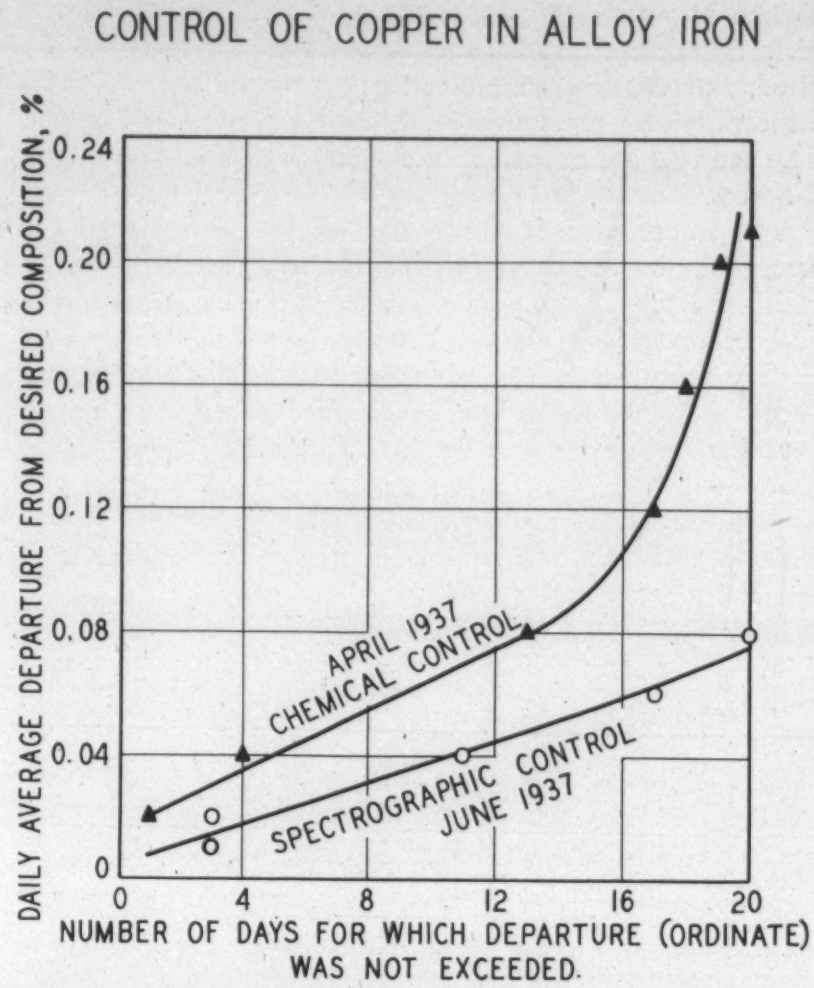


Fig. 12. Comparison of Production Records under Chemical and Spectrographic Control. Rapid and accurate spectrographic analysis shows marked improvement in uniformity of product.

A rapid and precise analysis procedure of the type described should show positive benefits in the accuracy to which production limits may be maintained, as has, indeed, proved to be true. Fig. 12 is a graph of the daily average variation in the copper content of copper-bearing irons, in production. The ordinates show the number of days during a selected month for which the variation did not exceed the percentages given as abscissae. The month selected for chemical control is thought to be typical; that for spectrographic control was the only full month available at the time the graph was drawn. The elimination of the larger variations is easily observed. Similar improvements have been shown in the control of other alloying elements.

Facts as to Actual Experience

Since the claims of spectroscopists in development laboratories sometimes fail to be realized when routine operation in a manufacturing plant is attempted, it should be borne in mind that the apparatus described has been installed at the foundry, that its speed and accuracy have been demonstrated by plant use, that the spectrographic laboratory is at present performing routine control analysis for all metallic alloying elements to the exclusion of chemical wet methods, and that the improved control permits the Campbell, Wyant & Cannon Foundry Co. to hold the variation in composition of their irons within narrower limits than was previously possible.

COMPARATIVE EFFECTS OF

Controlled Atmospheres

ON ALLOY AND CARBON STEELS

Part I

by E. E. Slowter and B. W. Gonser

Chemical Engineer and Metallurgist, Respectively, Battelle Memorial Institute, Columbus, Ohio.

THE SUCCESSFUL USE of cheap, partly burned gases as protective atmospheres for the heat treatment of plain low carbon steels has led to a demand for similar atmospheres for high carbon and special alloy steels. That the requirements for such atmospheres are far more exacting than when heat treating plain low carbon steels has long been recognized by heat treaters, atmosphere producer manufacturers and others concerned with these problems. It is seldom important to do bright hardening for appearance, but maintenance of dimensions against scaling is often important, while freedom from decarburization or the nuisance of having to remove a soft skin is ordinarily paramount. The term "bright hardening" or "clean hardening" is more often used than "non-decarburizing hardening" which is what is actually desired. We shall also use the shorter, though less precise, term.

Where clean hardening is to be done a variety of different alloy steels may have to be handled, hence the value of a given protective gas will depend, in part at least, on its suitability for use with alloy steels having a wide composition range. Fortunately, the greater value of the alloy steel products to be protected justifies a more expensive protective gas or more care in its preparation and purification.

It is known that highly alloyed steels may depart considerably from the behavior of plain carbon steels, both as to scaling and to decarburization. How marked these effects may be on the moderately alloyed steels that go into the bulk of heat-treated products is a matter that cannot be settled without some experimental evidence. The work here reported, which was done under the sponsorship of the Utilities Coordinated Research, Inc., and is published with the permission of the sponsor, is aimed to throw light on this question of how far some of the important alloy steels and plain carbon steels differ in their behavior toward various controlled atmospheres.

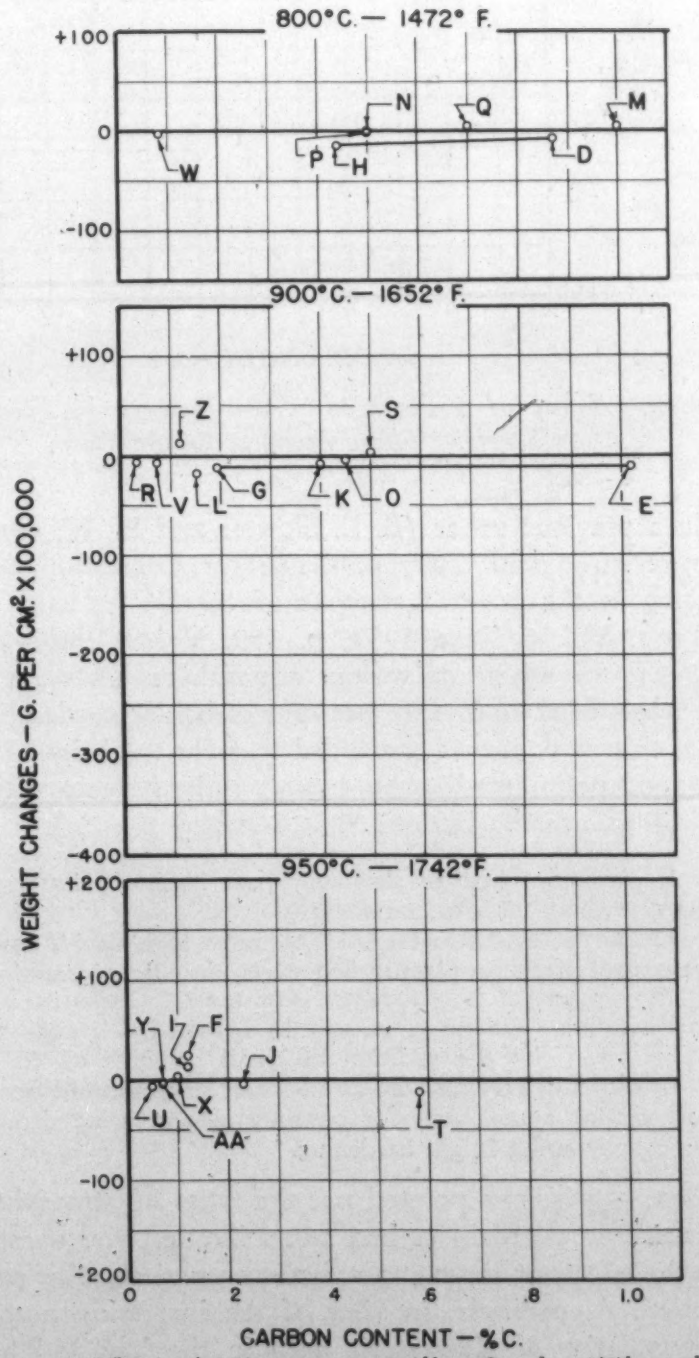


Fig. 1. Effect of Nitrogen on Alloy Steels. Three hours at temperature.

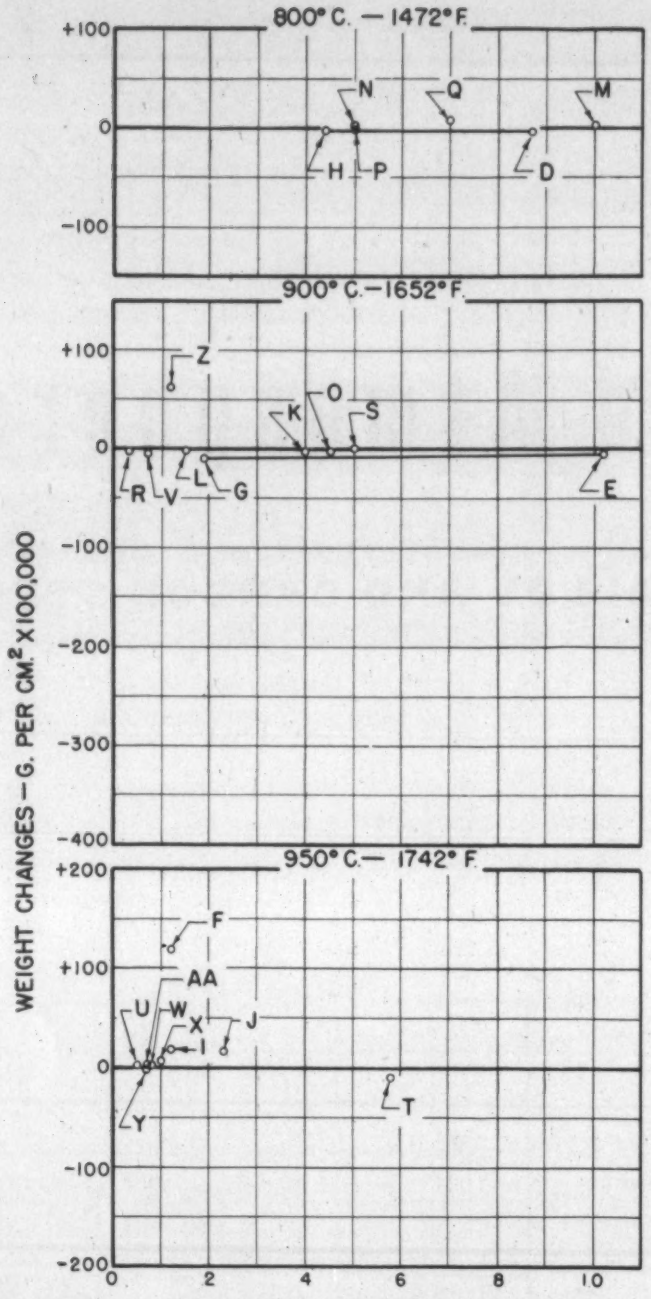


Fig. 2. Effect of 5 Per Cent CO—Balance N_2, Gas on Alloy Steels. Three hours at temperature.

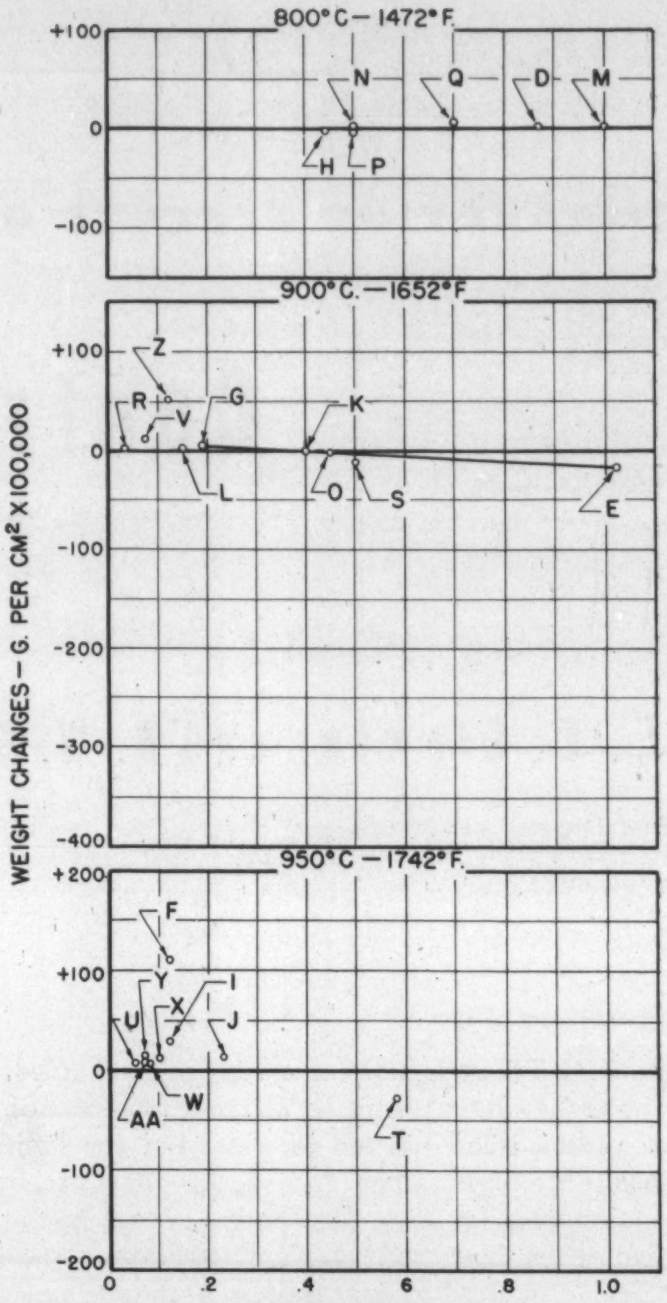


Fig. 3. Effect of 5 Per Cent CO — 0.3 Per Cent CH_4 — Balance N_2 Gas on Alloy Steels. Three hours at temperature.

In a previous paper (E. E. Slowter and B. W. Gonser, "An Experimental Study of Gases for Controlled Atmospheres in the Heat Treatment of Steel." METALS AND ALLOYS. Vol. 8, June 1937, p. 159. Vol. 8, July 1937, p. 195), the effects of various atmospheres on plain carbon steels of 0.07 to 1.02 per cent carbon were described. From this work it was concluded that for the bright hardening of plain, medium and high carbon steels without scaling or decarburization:

1. An atmosphere of absolutely pure N_2 is the least reactive with all plain carbon steels.
2. CO-N_2, H_2-N_2 and CO-H_2-N_2 gases high in N_2 have only small effects on plain carbon steels, the effects increasing as the amount of N_2 decreases. Any tendency towards decarburization by these gases may be balanced, for a given carbon steel, by the addition of small amounts of CH_4.
3. CO_2 and H_2O, as well as O_2, must be eliminated from heat-treating atmospheres for certainty in preventing decarburization during bright hardening.

These conclusions pointed out the types of atmospheres desirable for all plain carbon steels but left the question as to the effects of these atmospheres on various alloy steels unsettled. Accordingly, in view of the increasing number and popularity of alloy steels both in the low and high carbon ranges, a study was made of the action of some of the typical atmospheres on a group of alloy steels selected so as to cover most of the different types of alloys.

Types of Atmospheres Studied

The atmospheres selected for study were:

I. Synthetically prepared:
   a. Pure N_2
   b. 5 per cent CO, balance N_2
   c. 5 per cent CO, 0.3 per cent CH_4, balance N_2
   d. 10 per cent H_2, balance N_2
   e. 10 per cent H_2, 2 per cent CH_4, balance N_2
   f. 10 per cent CO, 10 per cent H_2, 1 per cent CH_4, balance N_2

II. Partly burned natural gas:
   a. Undried gas from generator:
      5 per cent CO_2, 10 per cent CO, 9 per cent H_2, 0.7 per cent CH_4, balance N_2
   b. Dried generator gas:
      5 per cent CO_2, 9 per cent CO, 9 per cent H_2, 1.0 per cent CH_4, balance N_2
   c. Dried, CO_2-free generator gas:
      9 per cent CO, 10 per cent H_2, 1 per cent CH_4, balance N_2

In each case, the gas composition given is that entering the heat-treating furnaces. These atmospheres are intended to represent a fair cross-section of the commercial possi-

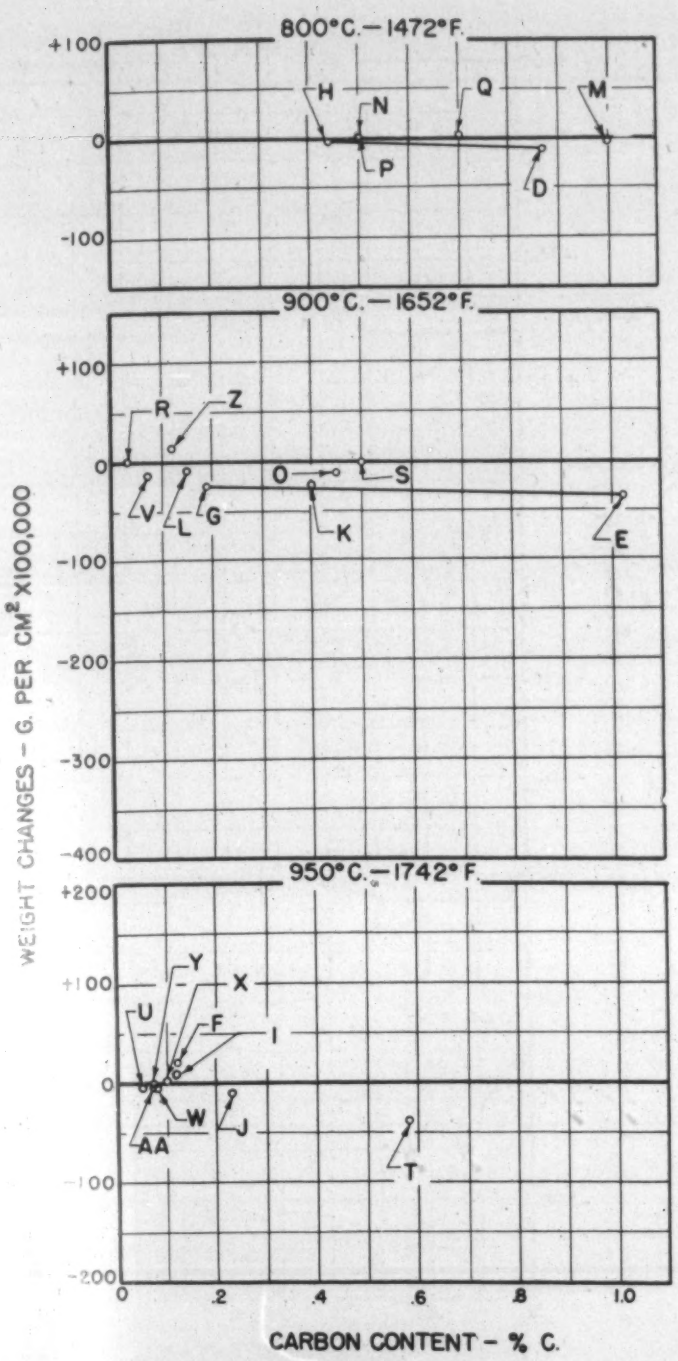


Fig. 4. Effect of 10 Per Cent H_2 — Balance N_2 Gas on Alloy Steels. Three hours at temperature.

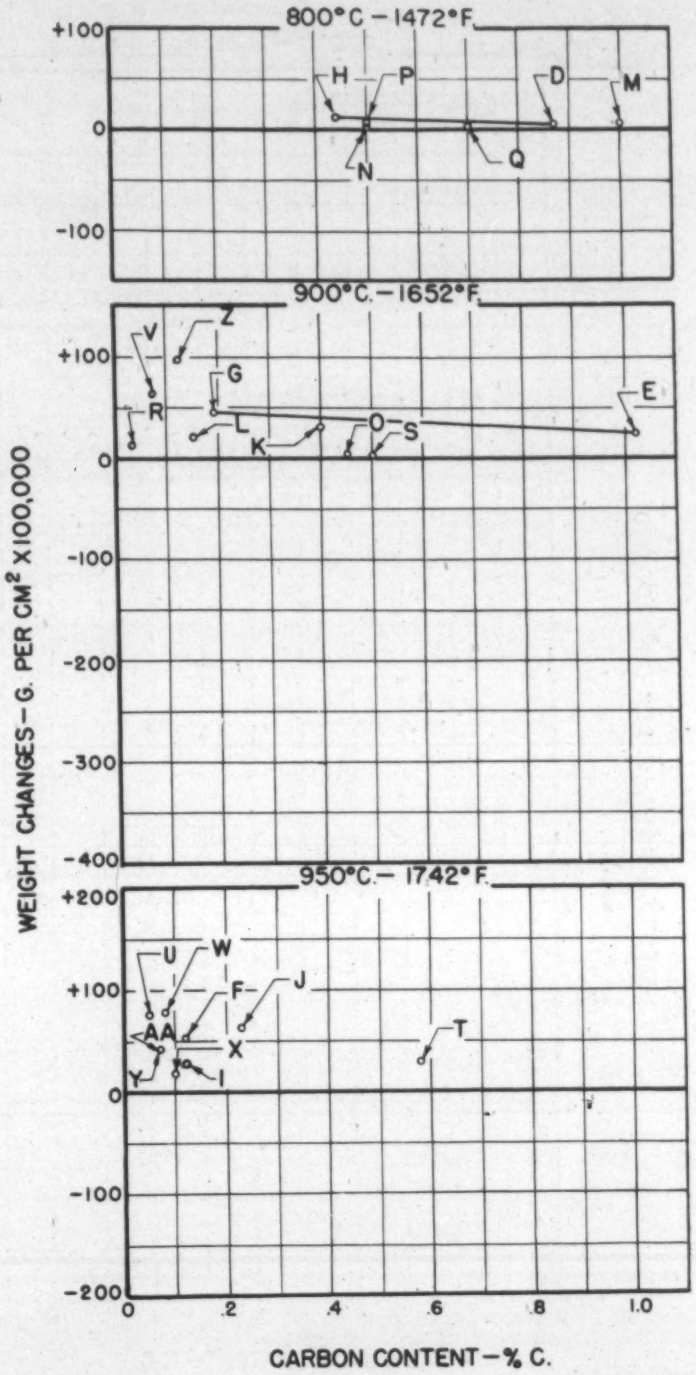


Fig. 5. Effect of 10 Per Cent H_2 — 2 Per Cent CH_4 — Balance N_2 Gas on Alloy Steels. Three hours at temperature.

bilities rather than to thoroughly cover all possible variations of any particular type of atmosphere. However, all do represent types of atmospheres which may be obtained if economically justified.

The synthetically prepared gases and the dried, CO_2-free generator gas represent that type of atmosphere which is non-reactive within itself, except for a slight breakdown by heat of any CH_4 that may be present. The undried and dried generator gases, however, represent that type of atmosphere which is reactive within itself when re-heated after its original preparation. The direction of these reactions is shown by the analyses in Table I.

Table I. Changes of Partly Burned Gas Atmospheres with Temperature

Source of Gas Sample	% CO_2	% CO	% H_2	% CH_4
Undried Generator Gas:				
Entrance to Furnace	5.1	9.7	9.0	0.7
Exit from Furnace at 1472 deg. F.	5.4	10.3	10.5	0.6
Exit from Furnace at 1652 deg. F.	4.6	11.9	10.3	0.6
Exit from Furnace at 1742 deg. F.	4.7	11.1	9.7	0.6
Dried Generator Gas:				
Entrance to Furnace	5.2	9.2	9.3	0.9
Exit from Furnace at 1472 deg. F.	4.1	10.8	9.3	1.0
Exit from Furnace at 1652 deg. F.	2.9	12.6	8.7	0.8
Exit from Furnace at 1742 deg. F.	2.9	12.4	8.5	0.9

The chief reaction taking place appears to be:

$$CO_2 + H_2 \rightleftarrows CO + H_2O$$

When the produced gas contains water, the reaction may be at or near a state of equilibrium when the gas is used. However, if the produced gas is thoroughly dried before use, the reaction is driven to the right at a speed dependent upon the annealing temperature used. This shows the futility of drying ordinary partly burned gas in order to eliminate the bad effects of water vapor except in the special cases where it is desired to bring the H_2/H_2O ratio of the entering gas to such a point that staining will not occur during cooling periods or where the annealing temperature is so low that the reaction does not take place to any appreciable extent. It should be remembered in this connection that superficial staining or temper colors are usually not objectionable with high carbon steels but that water vapor accelerates decarburization and this is most objectionable.

EXPERIMENTAL WORK

SINCE much work has been done on plain carbon steels and the atmospheres required for their protection, it seemed desirable to correlate the action of various alloy steels with the known actions of plain carbon steels so that

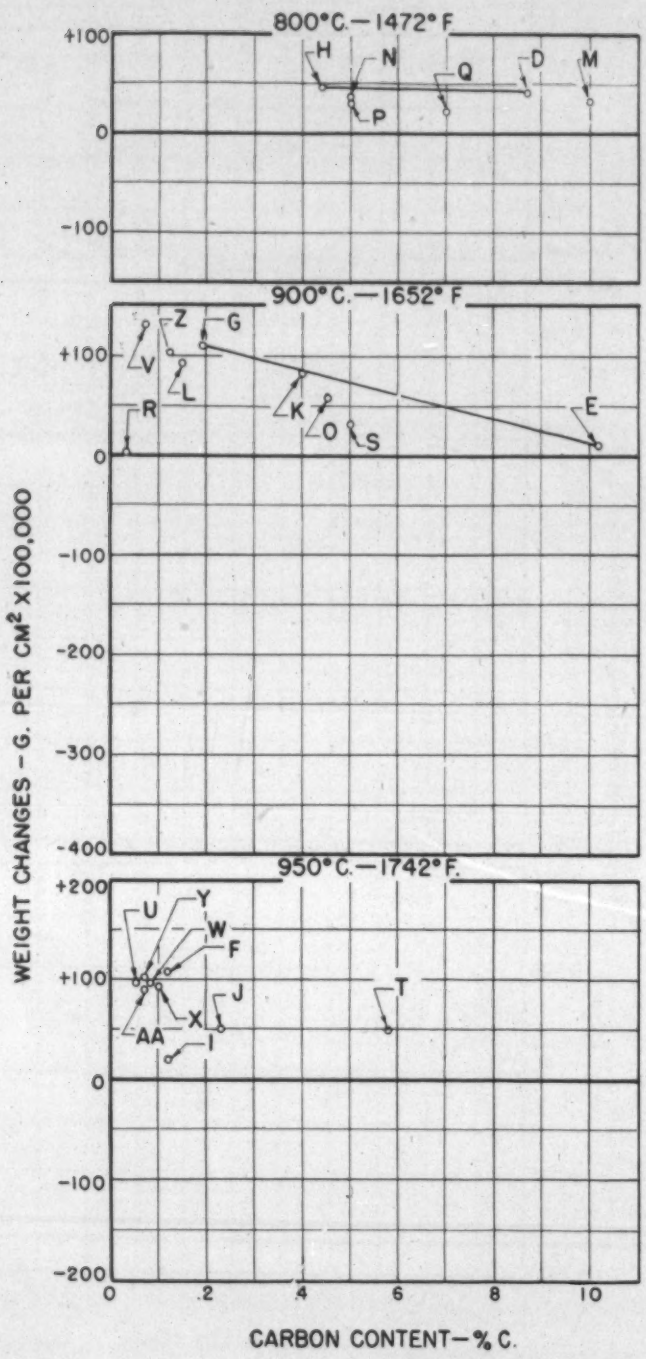


Fig. 6. Effect of 10 Per Cent CO — 10 Per Cent H_2 — 1 Per Cent CH_4 — Balance N_2 Gas on Alloy Steels. Three hours at temperature.

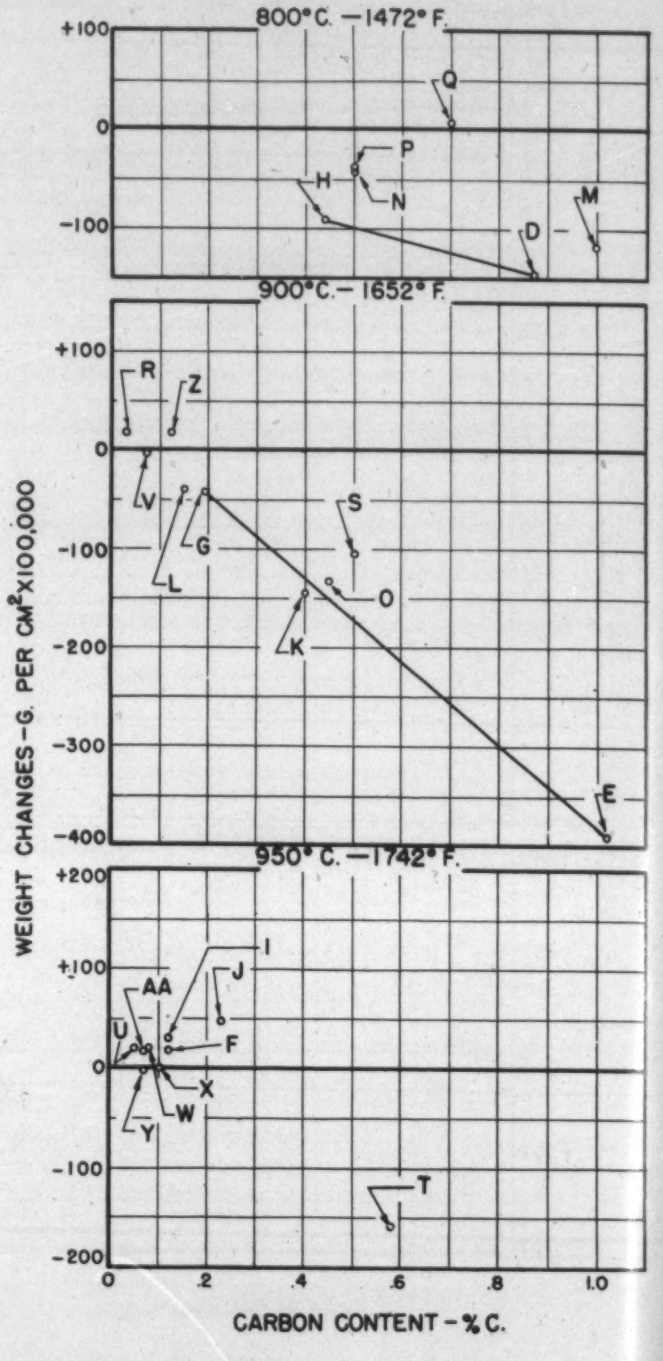


Fig. 7. Effect of Undried Generator Gas on Alloy Steels. Three hours at temperature.

Table II. Composition of Alloy Steels

Ident Letter	Type of Steel	C	Mn	P	S	Si	Cr	Mo	Ni	V	Cu	Al	W
					800° C.—1472° F. GROUP								
H	Plain carbon	0.44	0.73	0.016	0.040	0.18	....	....	....	....	....	....	....
N	SAE 3250—Ni-Cr.	0.50	0.45	0.04	0.045	....	1.10	....	1.75	....	....	....	....
P	SAE 2350—Nickel	0.50	0.65	0.04	0.05	....	....	....	3.5	....	....	....	....
Q	High speed drill rod	0.70	....	....	....	....	4.0	....	....	1.0	....	....	18.0
D	Plain carbon	0.87	0.49	0.040	0.032	0.24	....	....	....	....	....	....	....
M	SAE 52100—Chromium	1.00	0.35	0.03	0.035	....	1.35	....	....	....	....	....	....
					900° C.—1652° F. GROUP								
R	High silicon transformer sheet	0.03	....	....	....	3.5 to 4.25	....	....	....	....	....	....	....
V	Cu-Ni-Mo low alloy steel	0.07	0.82	0.013	0.03	0.002	....	0.093	0.92	....	1.38	....	....
Z	SAE 51710—Chromium	0.12	0.60*	0.030*	0.030*	0.50*	16-18	....	....	....	....	....	....
L	SAE 4615—Molybdenum	0.15	0.45	0.04	0.05	....	....	0.25	1.75	....	....	....	....
G	Plain carbon	0.19	0.91	0.018	0.154	0.15	....	....	....	....	....	....	....
K	SAE 4140—Molybdenum	0.40	0.65	0.04	0.05	....	0.95	0.20	....	....	....	....	....
O	SAE 6145—Cr-V	0.45	0.65	0.04	0.045	....	0.95	....	....	0.18	....	....	....
S	SAE 9250—Si-Mn	0.50	0.75	0.045	0.05	2.00	....	....	....	....	....	....	....
E	Plain carbon	1.02	0.29	0.016	0.027	0.18	0.04	....	0.036	....	0.083	....	....
					950°C.—1742° F. GROUP								
U	Ni-Cu low alloy steel	0.05	0.39	0.074	0.025	0.001	....	....	2.00	....	1.06	....	....
AA	Plain carbon	0.07	0.37	0.017	0.029	0.02	....	....	....	....	....	....	....
Y	Cu-Cr-Ni low alloy steel	0.07	0.42	0.01	0.023	0.224	0.69	....	0.45	....	0.80	....	....
W	Cu-Ni low alloy steel	0.08	0.48	0.12	0.024	0.13	....	....	0.47	....	1.05	....	....
X	Cr-Cu low alloy steel	0.10	0.22	0.173	0.026	0.93	1.14	....	....	....	0.36	....	....
I	Ni-Cr—Wire	0.12	....	....	....	....	20	....	80	....	....	....	....
F	Stainless (18-8)	0.12	....	....	....	....	18.0	....	8	....	....	....	....
J	Common nitriding steel	0.23	0.51	0.011	0.011	0.20	1.58	0.20	....	....	....	1.24	....
T	Copper steel	0.58	0.78	0.020	0.030	0.18	....	....	....	....	0.99	....	....

* Maximum, according to SAE specifications.

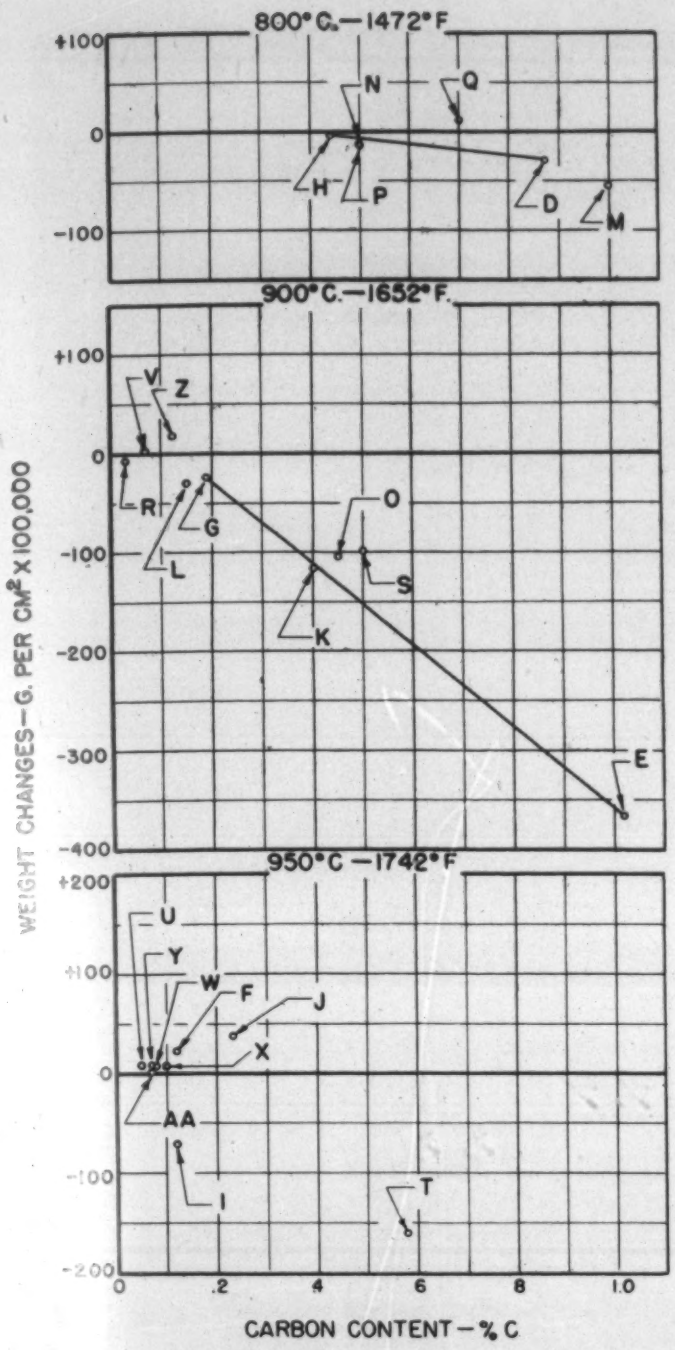


Fig. 8. Effect of Dried Generator Gas on Alloy Steels. Three hours at temperature.

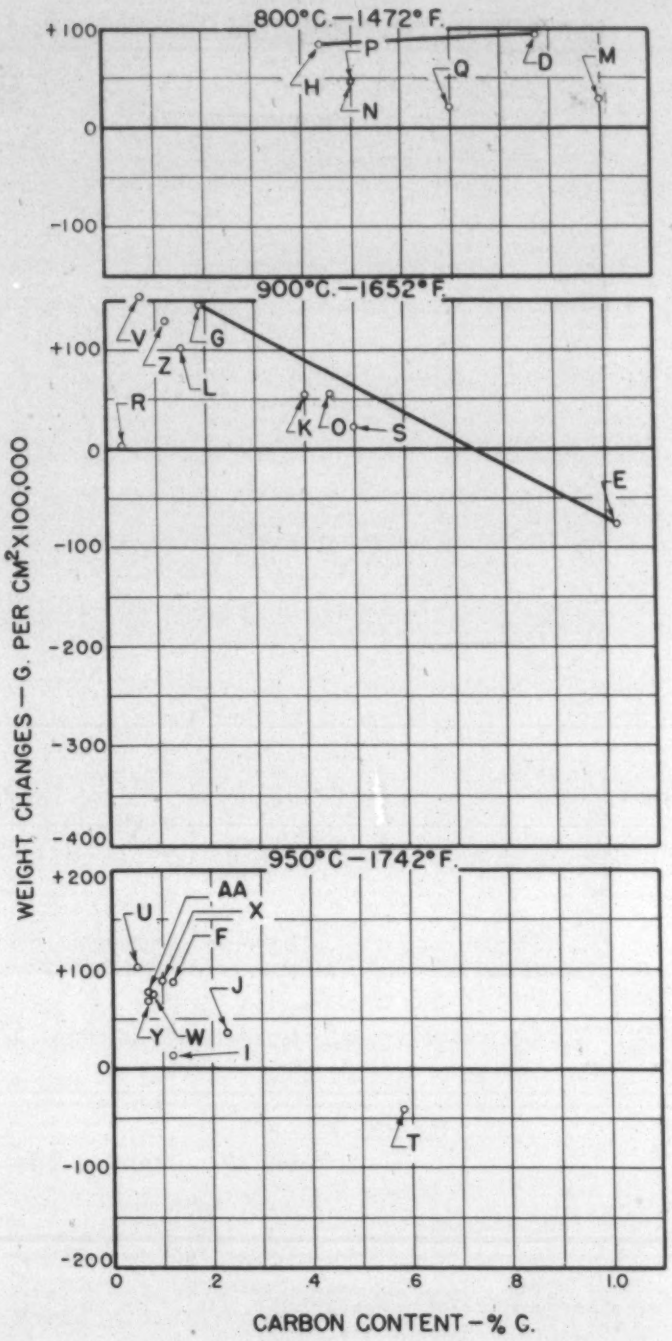


Fig. 9. Effect of Dried CO_2 — Free Generator Gas on Alloy Steels.

Table III. Effect of Various Atmospheres on Alloy Steels—Weight Changes in Grams per sq. Cm.

Ident. Letter	Type of Steel	Annealing Temperature	N_2	5% CO Bal. N_2	5% CO— 0.3% CH_4 Bal. N_2	10% H_2 Bal. N_2	10% H_2— 2% CH_4 Bal. N_2	10% CO— 10% H_2— 1% CH_4 Bal. N_2	Undried Generator Gas	Dried Generator Gas	Dried CO_2-Free Generator Gas
H	Plain carbon	800° C.	—0.00015	—0.00001	—0.00001	—0.00002	+0.00013	+0.00046	—0.00091	—0.00004	+0.00085
N	SAE 3250—Nickel-Chromium	1472° F.	0.00000	+0.00001	+0.00001	+0.00001	+0.00003	+0.00036	—0.00043	—0.00013	+0.00047
P	SAE 2350—Nickel	"	—0.00001	—0.00002	—0.00004	0.00000	+0.00006	+0.00030	—0.00038	—0.00016	+0.00049
Q	High speed drill rod	"	+0.00004	+0.00008	+0.00006	+0.00003	+0.00003	+0.00022	+0.00008	+0.00011	+0.00022
D	Plain carbon	"	—0.00007	—0.00002	+0.00001	—0.00011	+0.00006	+0.00042	—0.00147	—0.00027	+0.00094
M	SAE 52100—Chromium	"	+0.00003	+0.00003	+0.00002	—0.00003	+0.00006	+0.00031	—0.00118	—0.00054	+0.00029
R	High silicon transformer sheet	900° C.	—0.00007	—0.00002	+0.00002	0.00000	+0.00013	+0.00003	+0.00018	—0.00006	+0.00003
V	Cu-Ni-Mo low alloy steel	1652° F.	—0.00007	—0.00005	+0.00012	—0.00014	+0.00063	+0.00133	—0.00004	+0.00004	+0.00155
Z	SAE 51710—Chromium	"	+0.00012	+0.00064	+0.00051	+0.00013	+0.00097	+0.00105	+0.00017	+0.00017	+0.00131
L	SAE 4615—Molybdenum	"	—0.00021	—0.00002	+0.00002	—0.00009	+0.00021	+0.00094	—0.00041	—0.00030	+0.00102
G	Plain Carbon	"	—0.00013	—0.00011	+0.00005	—0.00026	+0.00047	+0.00112	—0.00043	—0.00024	+0.00146
K	SAE 4140—Molybdenum	"	—0.00010	—0.00003	0.00000	—0.00024	+0.00031	+0.00084	—0.00145	—0.00117	+0.00055
O	SAE 6145—Chromium-Vanadium	"	—0.00003	—0.00002	—0.00001	—0.00012	+0.00004	+0.00058	—0.00134	—0.00105	+0.00056
S	SAE 9250—Silico Manganese	"	+0.00003	0.00000	—0.00012	—0.00001	+0.00003	+0.00031	—0.00104	—0.00099	+0.00023
E	Plain carbon	"	—0.00012	—0.00005	—0.00018	—0.00035	+0.00024	+0.00011	—0.00389	—0.00366	—0.00076
U	Ni-Cu low alloy steel	950° C.	—0.00008	+0.00001	+0.00007	—0.00006	+0.00076	+0.00096	+0.00021	+0.00007	+0.00101
AA	Plain carbon	1742° F.	—0.00006	+0.00003	+0.00007	—0.00005	+0.00042	+0.00090	+0.00017	+0.00001	+0.00076
Y	Cu-Cr-Ni low alloy steel	"	—0.00003	0.00000	+0.00013	—0.00001	+0.00041	+0.00102	—0.00003	+0.00007	+0.00068
W	Cu-Ni low alloy steel	"	—0.00002*	+0.00001	+0.00006	—0.00005	+0.00078	+0.00096	+0.00019	+0.00007	+0.00074
X	Cr-Cu low alloy steel	"	+0.00002	+0.00007	+0.00011	+0.00001	+0.00019	+0.00093	0.00000	+0.00007	+0.00088
I	Ni-Cr wire	"	+0.00011	+0.00018	+0.00027	+0.00008	+0.00027	+0.00020	+0.00031	—0.00071	+0.00012
F	Stainless (18-8)	"	+0.00022	+0.00119	+0.00110	+0.00020	+0.00053	+0.00107	+0.00017	+0.00023	+0.00086
J	Common nitriding steel	"	—0.00005	+0.00016	+0.00013	—0.00010	+0.00064	+0.00051	+0.00048	+0.00037	+0.00036
T	Copper steel	"	—0.00013	—0.00010	—0.00027	—0.00039	+0.00029	+0.00050	—0.00160	—0.00160	—0.00042

* 800° C.-1472° F. for this run only.

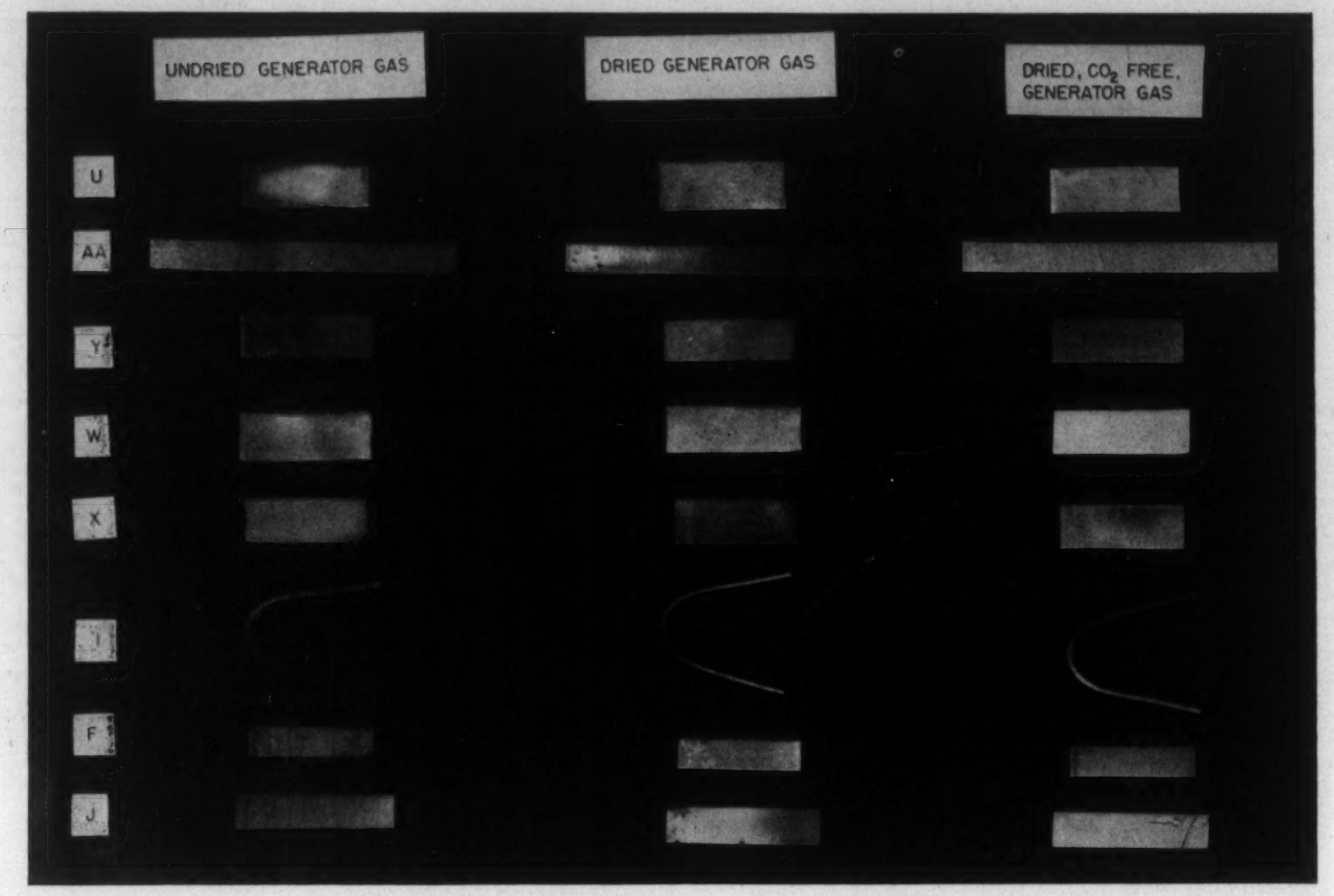


Fig. 10. Comparison of Appearance of Selected Steel Specimens after Heating 3 Hrs. at 950 Deg. C. (1742° F.).

Table IV. Staining Effects of Various Atmospheres on Alloy Steels

Ident. Letter	Type of Steel	Annealing Temperature	N_2	5% CO Bal. N_2	5% CO— 0.3% CH_4 Bal. N_2	10% H_2 Bal. N_2	10% H_2— 2% CH_4 Bal. N_2	10% CO— 10% H_2 1% CH_4 Bal. N_2	Undried Generator Gas	Dried Generator Gas	Dried CO_2-Free Generator Gas
H	Plain carbon	800° C.	B-1	0	A-1	0	0	A-1	B-4	B-4	B-3
N	SAE 3250—Nickel-Chromium	1472° F.	B-2	A-1	C-1	C-2	C-1	C-2	B-3	B-3	C-2
P	SAE 2350—Nickel	"	0	0	A-1	0	0	A-1	B-3	B-4	A-1
Q	High speed drill rod	"	C-1	C-2	C-3	C-2	C-2	C-2	B-4	B-4	C-3
D	Plain carbon	"	B-1	0	A-1	0	A-1	A-1	B-3	B-3	B-2
M	SAE 52100—Chromium	"	C-3	C-1	C-2	C-2	C-1	C-2	B-3	B-3	C-3
R	High silicon transformer sheet	900° C.	B-1	A-1	A-1	A-1	A-2	A-1	B-2	B-2	A-2
V	Cu-Ni-Mo low alloy steel	1652° F.	0	0	0	A-1	0	0	B-3	B-3	B-2
Z	SAE 51710—Chromium	"	C-3	C-3	C-3	C-1	A-3	C-2	C-3	C-3	C-1
L	SAE 4615—Molybdenum	"	B-1	A-1	A-1	0	0	A-1	B-3	B-4	A-1
G	Plain carbon	"	B-2	0	A-1	A-1	0	A-1	B-3	B-3	B-1
K	SAE 4140—Molybdenum	"	C-2	C-1	C-2	0	0	C-3	B-3	B-3	C-4
O	SAE 6145—Chromium-Vanadium	"	B-1	A-3	A-3	A-1	A-1	A-4	B-3	B-3	A-3
S	SAE 9250—Silico-Manganese	"	A-1	A-2	A-2	A-2	A-2	A-2	A-3	A-3	A-2
E	Plain carbon	"	B-1	A-1	A-1	0	0	A-1	B-3	B-3	B-2
U	Ni-Cu low alloy steel	950° C.	B-1	0	0	0	A-1	0	B-3	B-3	0
AA	Plain carbon	1742° F.	B-1	0	0	0	A-1	0	B-3	B-2	0
Y	Cu-Cr-Ni low alloy steel	"	B-1	C-1	C-2	C-3	A-1	B-3	B-4	B-3	A-3
W	Cu-Ni low alloy steel	"	B-1	A-1	A-1	A-1	A-1	A-1	B-2	B-3	A-1
X	Cr-Cu low alloy steel	"	B-1	C-2	C-2	C-1	C-2	C-2	B-3	B-4	C-2
I	Ni-Cr wire	"	C-1	C-2	C-1	C-1	C-1	C-2	C-3	C-3	C-3
F	Stainless (18-8)	"	C-3	C-3	C-3	C-3	A-2	C-3	C-3	C-3	C-3
J	Common nitriding steel	"	B-1	A-3	A-3	C-2	A-1	A-2	B-4	B-4	A-2
T	Copper steel	"	B-1	A-1	A-1	A-1	A-1	A-1	B-4	B-4	A-1

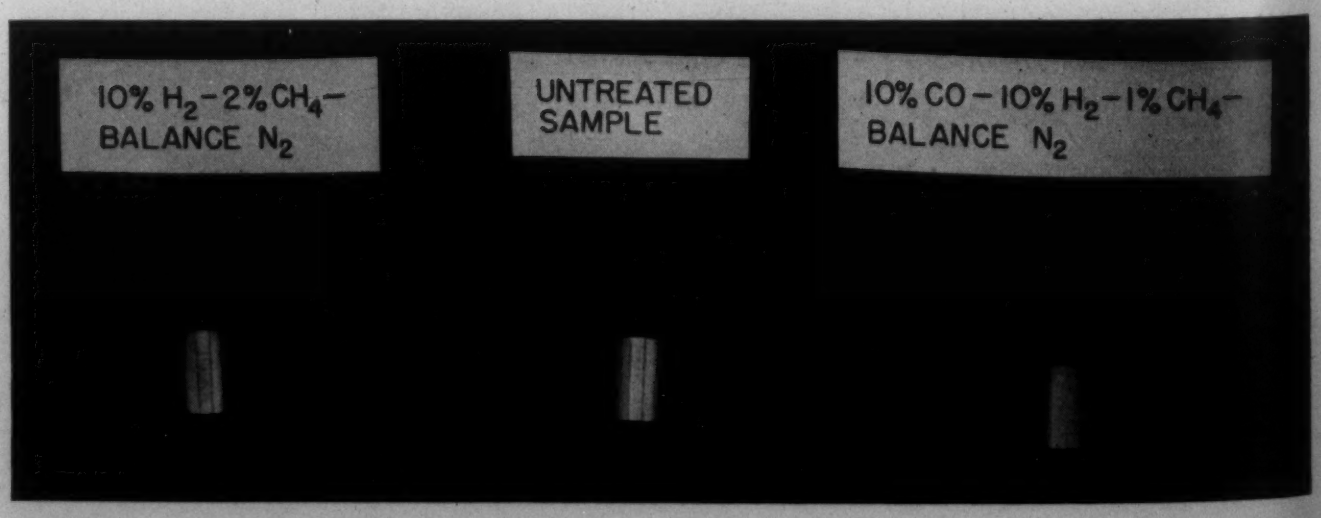


Fig. 11. Appearance of Specimen E, a High Carbon Steel, before and after 3 Hrs. at 900 Deg. C. (1652° F.). No decarburization.

all types of atmospheres would not have to be tried each time it was necessary to heat treat a new alloy steel.

Materials and Procedure

As in the previous work on plain carbon steel, cylinder H_2 and N_2, gasometer CO prepared from formic and sulphuric acids and methane as natural gas (70% CH_4, 10% C_2H_6, 4% C_3H_8, Bal. = N_2, CO_2 and O_2) were used as the gas sources for the synthetic mixtures. Suitable purification methods were selected to assure the removal of residual O_2, CO_2 and water vapor. These gases were measured by calibrated orifices and mixed to the desired proportions. The partly burned gas was prepared in a standard type of generator from natural gas and air. In either case the product gas was conveyed at the rate of approximately 150 c.c. per min. to each of three heat-treating furnaces (vol. = 475 c.c. each) which were operated simultaneously but at different temperatures.

The grouping and analyses of the steels used are shown in Table II. Not all the important commercial alloy steels were tested but an attempt was made to cover a fair cross section of the field. The analyses given in this table represent a combination of analyses actually made and analyses furnished by the makers of the various steels. In practice these specimens, after machining to shape, were further cleaned and polished with emery paper, washed in alcohol, dried and weighed before insertion in the proper furnaces. After insertion of the samples, the cold furnaces were purged from free O_2 with the particular gas under consideration. The furnaces were then brought to their respective temperatures and held at that point for 3 hrs., after which the specimens were allowed to cool in the gas stream. After cooling, the samples were re-weighed. From these data the weight change per unit area was calculated for each type of steel.

The samples were separated into three temperature groups, each sample being placed into that group whose temperature most nearly corresponded with the ordinary heat-treating temperature for that particular steel. A plain carbon steel in each group served to correlate results with these alloy steels and previous work on plain carbon steels. A three hour period at temperature was selected so as to exaggerate and emphasize any weight changes which were taking place. Under most commercial conditions this time of treatment would of course be much shorter. This point should be remembered throughout the whole discussion.

For quantitative measurement the results have been reported in weight change per unit area for each sample. Positive values are considered to represent carburization and negative values, decarburization. This is not strictly true for those cases where staining occurred but even then is sufficiently accurate for comparative results. It has been previously found that, for all practical purposes, weight changes of ± 0.00010 g. per sq. cm. were negligible in showing any effect of an atmosphere upon any given steel.

Results

The weight changes for each type of steel in each of the atmospheres used are given in Table III. These results are shown graphically in Figs. 1 to 9, inclusive. In these figures each point represents a given type of steel. Where two plain carbon steels are present in the same group, a straight line has been drawn between the two points representing these plain carbon steels. Table IV shows the staining effects of the various atmospheres on the steels. These ratings represent the average of the estimates of three observers. The key to the system of rating is as follows:

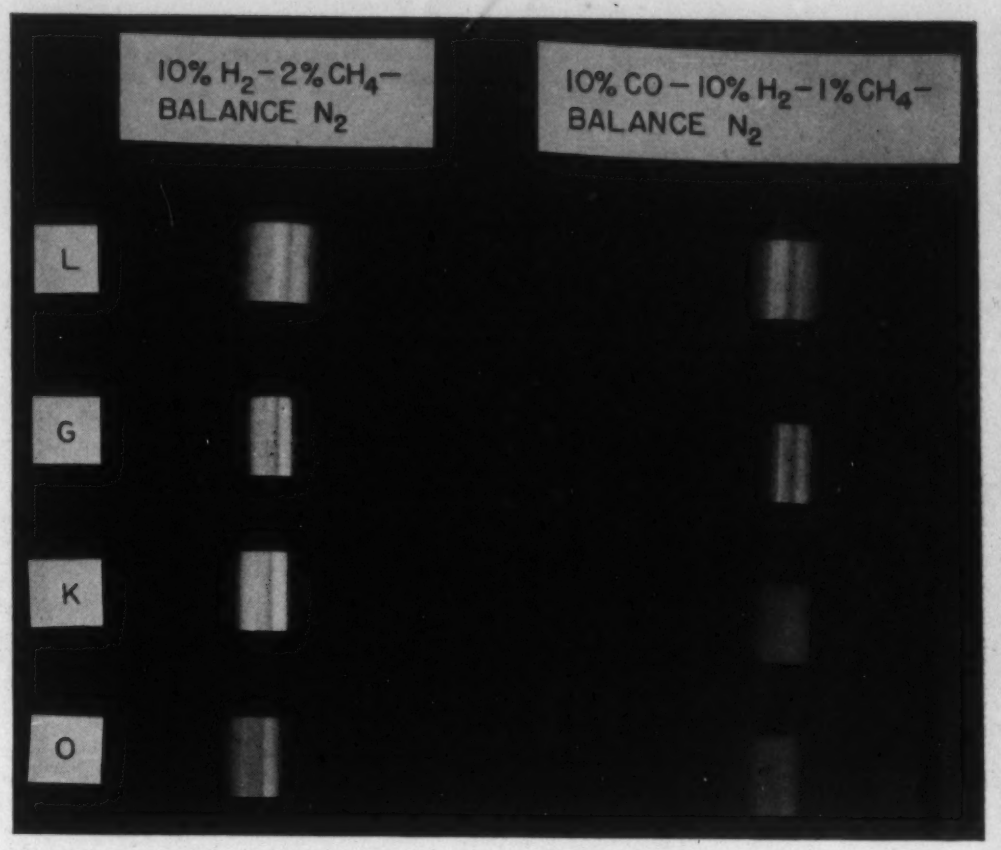


Fig. 12. Effect of CO on Appearance of Steels Containing 0.95 Per Cent Cr. Specimens L and G are Cr-free; K and O containing Cr may be bright hardened in H_2 but not in presence of CO.

O= No effect.

A-1 = Slightly reduced reflectivity	B-3 = Blue surface
A-2 = Slight fog	B-4 = Blue-black surface
A-3 = Gray fog	C-1 = Thin green film
A-4 = Heavy gray fog	C-2 = Green film
B-1 = Partial blue staining	C-3 = Heavy green film
B-2 = Thin blue film	C-4 = Green fog

The appearance of a group of steel specimens after heating for 3 hrs. at 950 deg. C. (1742 deg. F.) is shown by Fig. 10. Unfortunately, in photographing and in the reproduction of such illustrations, considerable shade differentiation is lost, and coloration, as the characteristic greenish tint due to oxidized chromium, is lost entirely. The dark shades of alloys *y*, *x*, *i*, and *f* are traceable to their chromium contents. Alloy *j* after treatment in dry CO_2-free generator gas, appears white in the photograph but it has a slightly fogged coating, whereas alloys *u*, *aa* and *w* are bright.

That really bright hardening of high carbon steels is possible without decarburization is shown by Figs. 5, 6 and 11. With the 10 per cent H_2 — 2 per cent CH_4 gas no noticeable effect was apparent although the photograph indicates slightly less reflectivity; with the 10 per cent CO — 10 per cent H_2 — 1 per cent CH_4 gas the surface was bright but reflectivity was dimmed by a noticeable slight fog. Steels containing about 1 per cent of chromium or more are rather severely fogged by gases containing CO, as shown by Fig. 12. The presence of any oxygen-containing gas, i. e. CO, CO_2 or free O_2, prevents a bright surface on high chromium steels under conditions covered by these tests.

(To be concluded)

[*Part II will include a discussion of the results with photomicrographs.—Editor.*]

NOTE ON SHORT-TIME

High-Temperature Tensile Tests

OF WROUGHT NI-CR ALLOYS

by Kenneth E. Quier

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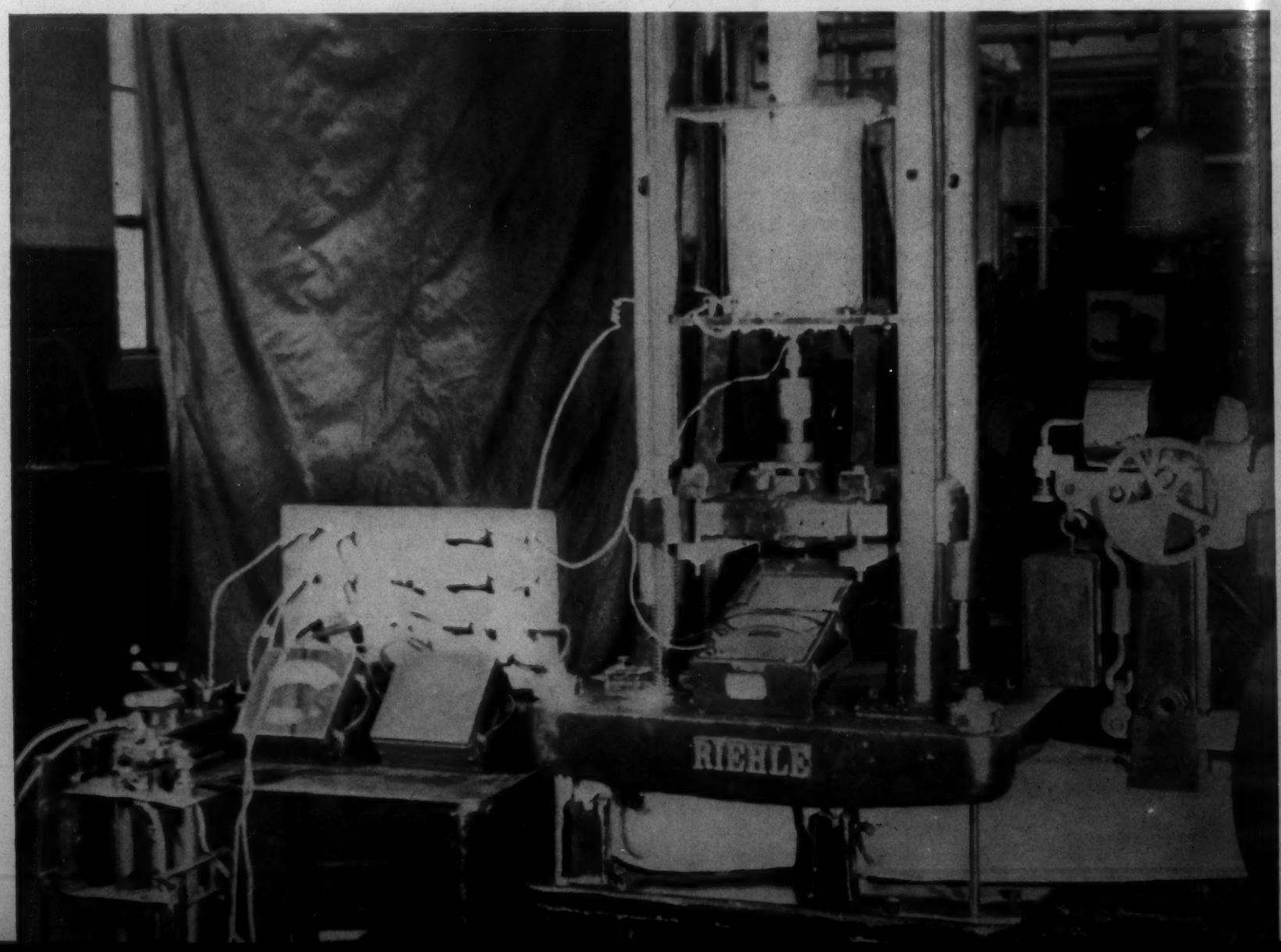
Pratt Institute, Brooklyn, N. Y.

Condensed from a thesis submitted by the author in partial fulfillment of the requirements for the degree of Master of Mechanical Engineering at the Polytechnic Institute of Brooklyn.

THE ALLOYS EMPLOYED for electrical resistance wires are sometimes used in wrought form for the fabrication of load-carrying parts for high-temperature service. While creep studies are necessary for the evaluation of the long-time load-carrying ability, the ability to survive a sudden over-load is also important, and this may be approximately determined by short-time high-temperature tensile tests.

Two commercial resistor alloys, furnished by the Wilbur B. Driver Co, Newark, N. J., and known as "Tophet A" (80% Ni, 20% Cr) and "Tophet C" (60% Ni, 16% Cr,

Fig. 1.—Tension Testing and Heating Equipment Employed.



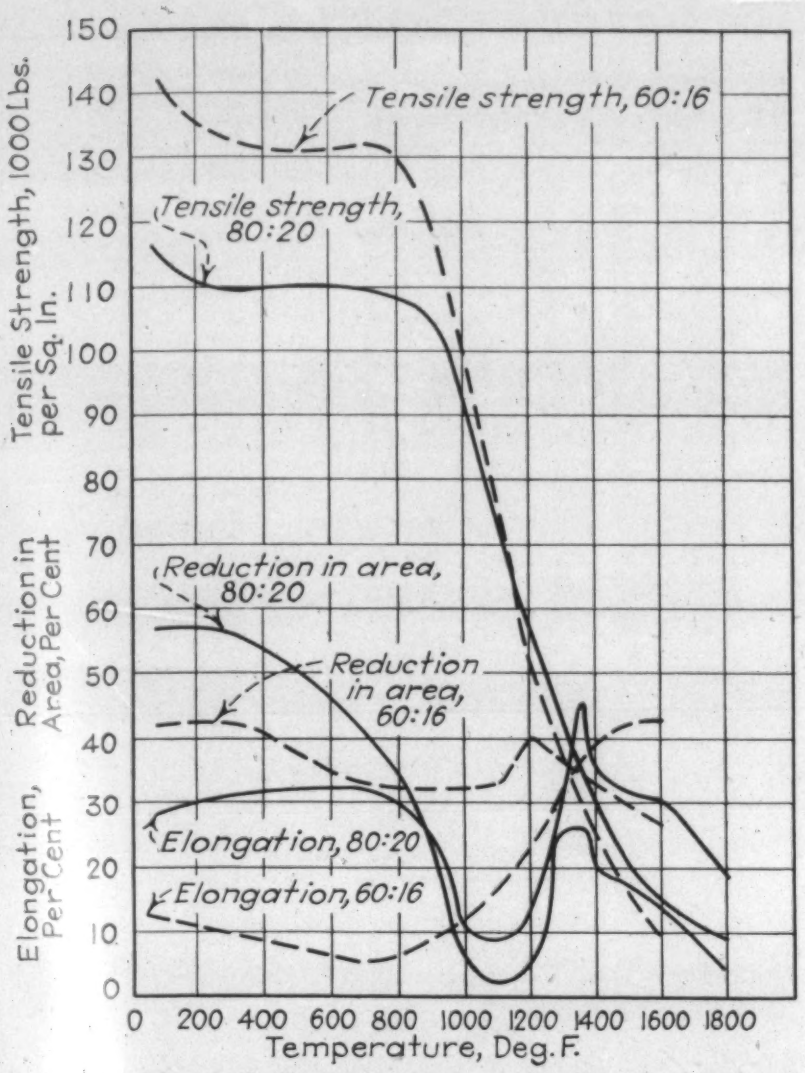

Tensile Strength, 1000 Lbs. per Sq. In.
Reduction in Area, Per Cent
Elongation, Per Cent
Tensile strength, 60:16
Tensile strength, 80:20
Reduction in area, 80:20
Reduction in area, 60:16
Elongation, 80:20
Elongation, 60:16
Temperature, Deg. F.
0 200 400 600 800 1000 1200 1400 1600 1800
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150

Fig. 2.—Effect of Temperature on the Tensile Strength, Reduction of Area and Elongation of Tophet A (80 Ni, 20 Cr) and Tophet C (60 Ni, 16 Cr, Remainder Fe). Solid lines are 80:20; dotted lines, 60:16.

remainder Fe) were subjected to short-time high temperature tensile tests, the former up to 1800 deg. F., the latter to 1600 deg. F.

Materials and Testing Procedure

The largest rod available was ¼ in. diam. The test specimens therefore had to be of substandard size. However a gage length and diameter of 0.75 in. long and 0.167 in. diam., proportional to those of a standard test bar, were chosen. Otherwise, the testing equipment and procedure conformed to the standards of the American Society for Testing Materials (A.S.T.M.—E21-34T).

The furnace was gap-wound and calibration tests on bars of each alloy showed the temperature distribution over the gage length to be within 2 deg. up to 1400 deg. F. and within 5 deg. at 1400 deg. F. and above. The furnace was so mounted that it moved with the movable head of the testing machine. The specimens were brought to temperature and held there 20 min. before starting the test. The motion of the head of the testing machine was 0.05 in. per min. The set-up is shown in Fig. 1.

The materials were not analyzed chemically; their compositions were obtained, however, from the foundry melting records of the heats from which the respective samples were drawn. These "charged analyses" are given in Table I.

Both alloys are low-carbon materials, the carbon content of Tophet A being 0.04-0.08 per cent and that of Tophet C 0.06-0.12 per cent, according to frequent checks.

The stock in each case had been hot-rolled to ¼ in. and then thoroughly annealed.

Table 1. Composition of the Alloys Investigated by Pilling and Worthington, and by the Author.

Material	Composition, Per Cent Ni	Cr	Fe	Mn	Si	C
80:20						
Pilling & Worthington's No. 5	79.7	19.04	0.88	..	0.10	0.09
Pilling & Worthington's No. 6	Bal.	19.80	0.48	2.3	0.30	0.13
Author's Tophet A.....	76.75	20.50	0.50	1.0	1.25	0.08 max.
60:16						
Pilling & Worthington's No. 3	60.3	15.90	Bal.	2.4	0.09	0.14
Author's Tophet C.....	59.0	16.00	21.25	2.5	1.25	0.12 max.

Test Results

The results of the tests over the range 300-1800 deg. F. are given in Fig. 2; the testing temperatures were, for Tophet A:72, 300, 500, 750, 900, 1000, 1100, 1200, 1300, 1350, 1400, 1600 and 1800 deg. F., and for Tophet C: 72, 300, 500, 750, 900, 1000, 1100, 1200, 1400 and 1600 deg. F. Neither yield strength nor proportional limit was determined.

The Tophet A results are given by the solid lines in Fig. 2. The plotted points are averages; from 2 to 4 specimens were used at each temperature, and any specimen fracturing at the fillet was discarded, only those being plotted from fractures within the middle 2/3 of the gage length. Individual observations on tensile strength agreed closely, as did those for elongation and reduction of area up to 1400 deg. F. At 1400 and 1600 deg. F. the ductility figures on duplicate bars showed wide divergence, but agreed well again at 1800 deg. F. The scatter at 1400 and 1600 deg. F. is shown in Table II, which gives results for each Tophet A specimen tested at those temperatures.

Table II. Ductility Values Observed for Individual Tophet A Specimens at 1400 and 1600 deg. F.

Temperature, deg. F.	Reduction in Area, Per Cent	Elongation, Per Cent
1400	25.40	41.20
	22.70	29.10
	13.85	21.78
1600	23.70	40.60
	9.05	20.30

The results on Tophet C are shown by the dotted lines in Fig. 2. Only one specimen was tested at each temperature in this series.

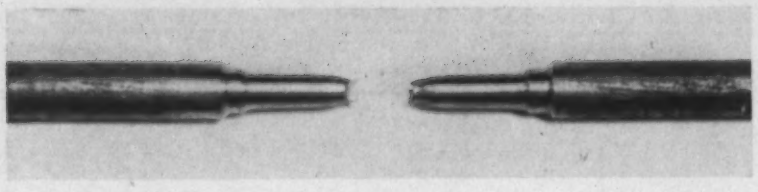
The fractures of the Tophet A specimens are given in Fig. 3 and those of the Tophet C in Fig. 4.

Discussion of Results

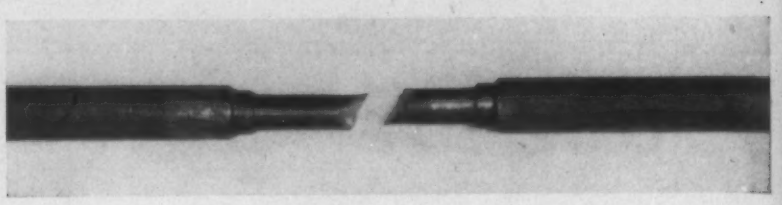
The 80:20 alloy shows a deep valley in ductility from 900 to 1300 deg. F., falling to a minimum at 1100 deg. F., but recovering sharply at 1300 deg. F., after which the ductility falls off again. Its fracture was intra-crystalline up to 1200 deg. F., but inter-crystalline from 100 to 1800 deg. F. Some grain growth was noted at 1600 deg. F. and pronounced grain growth at 1800 deg. F. The change in grain size with rising testing temperature is illustrated in Fig 5.

The brittle range noted with 80:20 was not so marked in the higher iron alloy, Tophet C. Some inter-crystalline cracking was also observed in the fractures of the latter at 1400 and 1600 deg. F.

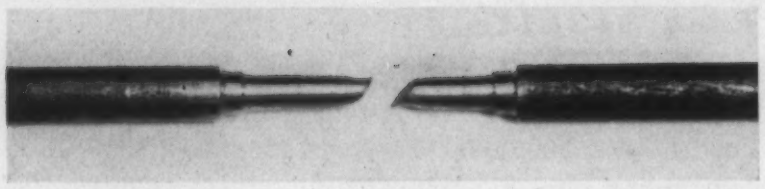
Pilling and Worthington (A.S.T.M.—A.S.M.E. Joint Symposium on Effect of Temperature on the Properties of Metals, 1931, page 502) have given data for 2 alloys of the 80:20 type. In Fig. 6 their data are plotted on the same coordinates as the author's values. Pilling and Worthington's material No. 6 (which contained 2.3% Mn) showed the 1000-1200 deg. F. dip in ductility but did not fall again. Their material No. 5 (which contained little or



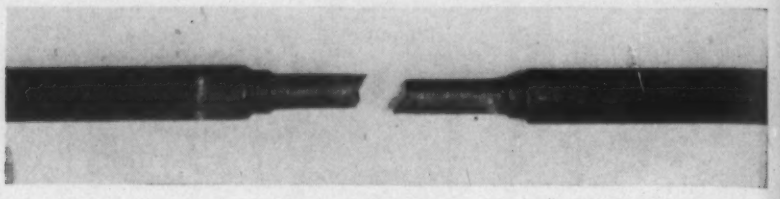
A-5 72° F.



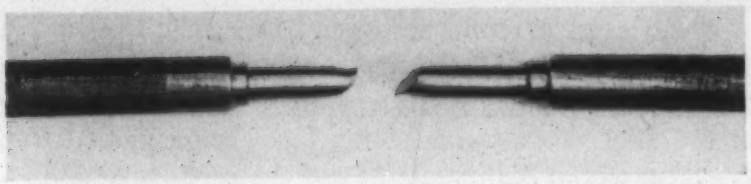
A-25 1100° F.



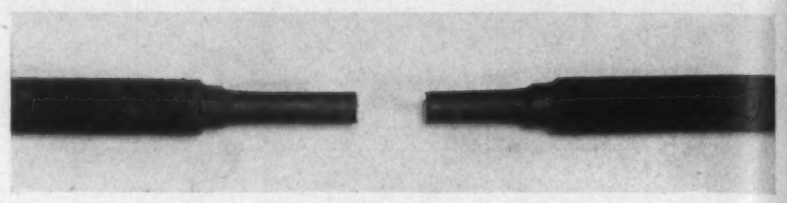
A-7 300° F.



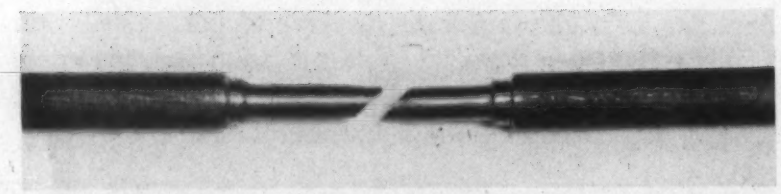
A-23 1200° F.



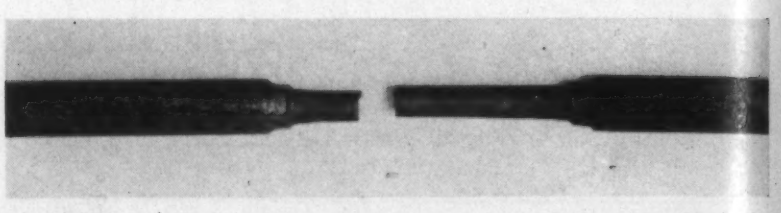
A-16 500° F.



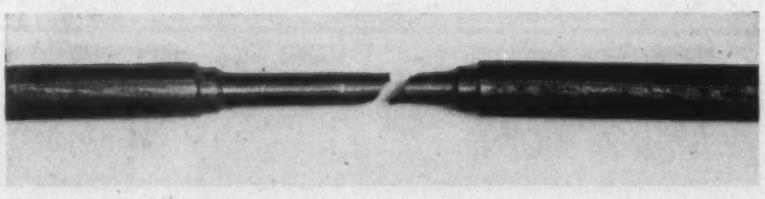
A-27 1350° F.



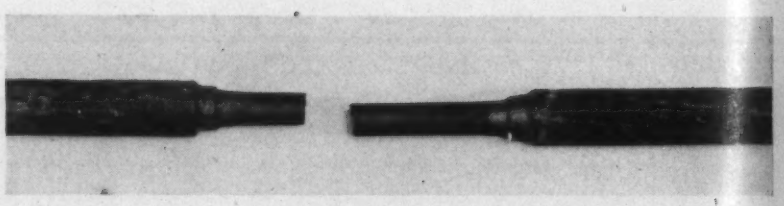
A-17 750° F.



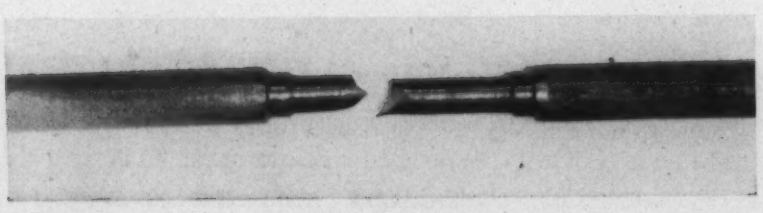
A-15 1400° F.



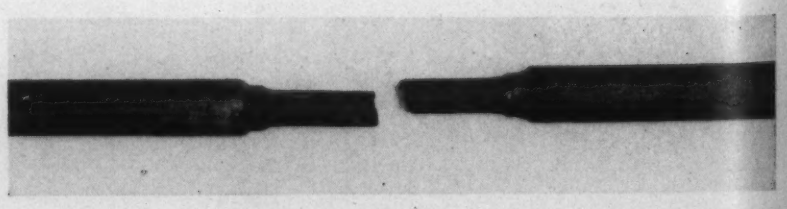
A-1 900° F.



A-26 1600° F.



A-19 1000° F.



A-29 1800° F.

Fig. 3.—Fractures of the 80:20 Alloy at Various Testing Temperatures.

no Mn) did not fall off in ductility so soon, fell to about the same level as No. 6 at a higher temperature, and did not appreciably rise thereafter. The author's curves for Tophet A (which contained about 1% Mn) are almost the resultant of Pilling and Worthington's Nos. 5 and 6. Although this evidence is probably insufficient to prove any correlation between manganese content and the ductility of 80:20 alloy in this "brittle range," it does show that rather small changes in composition or in melting practice can profoundly affect the ductility of this type of material.

Pilling and Worthington also give data for an alloy of the 60:16 class, which are plotted in Fig. 7 together with the author's curves for Tophet C. Their alloy (Material No. 3) was weaker and more ductile at room temperature than the Tophet C used in the present work. The tensile strengths of the two lots became of the same order at 1300-1600 deg. F., while the elongation and reduction of area values agree fairly well in that temperature range.

The change in the relative tensile strengths of the 80:20 and 60:16 alloys at various temperatures is also worthy of note. Pilling and Worthington found the 80:20 alloy to be of superior strength at all temperatures, whereas the author found the 80:20 to be weaker than the 60:16 alloy below 1150 deg. F., and stronger, and increasingly so in comparison, as the temperature rose above this value. At

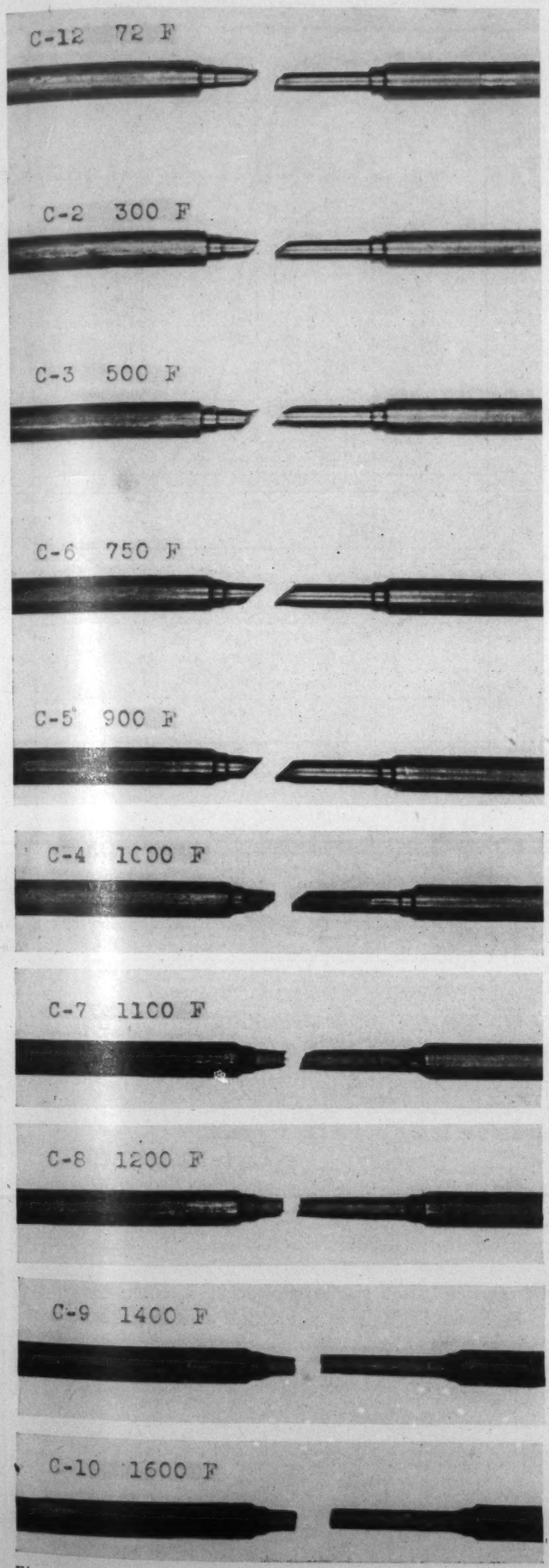
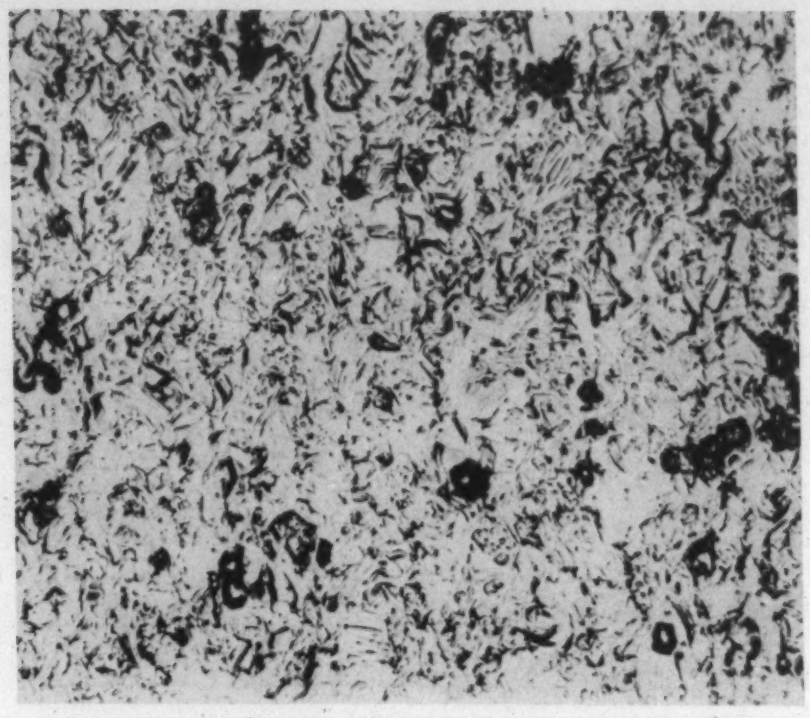
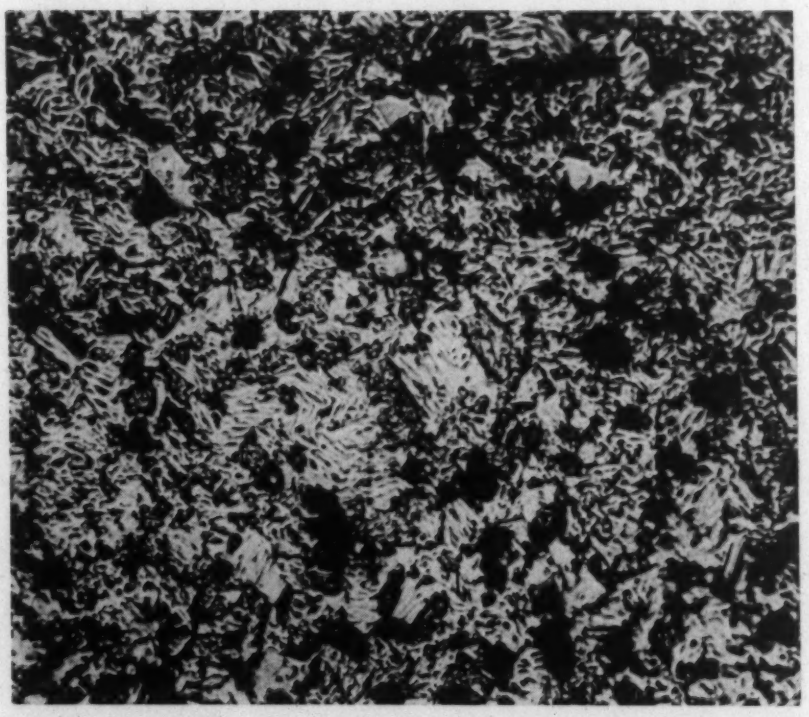


Fig. 4.—Fractures of the 60:16 Alloy at Various Testing Temperatures.





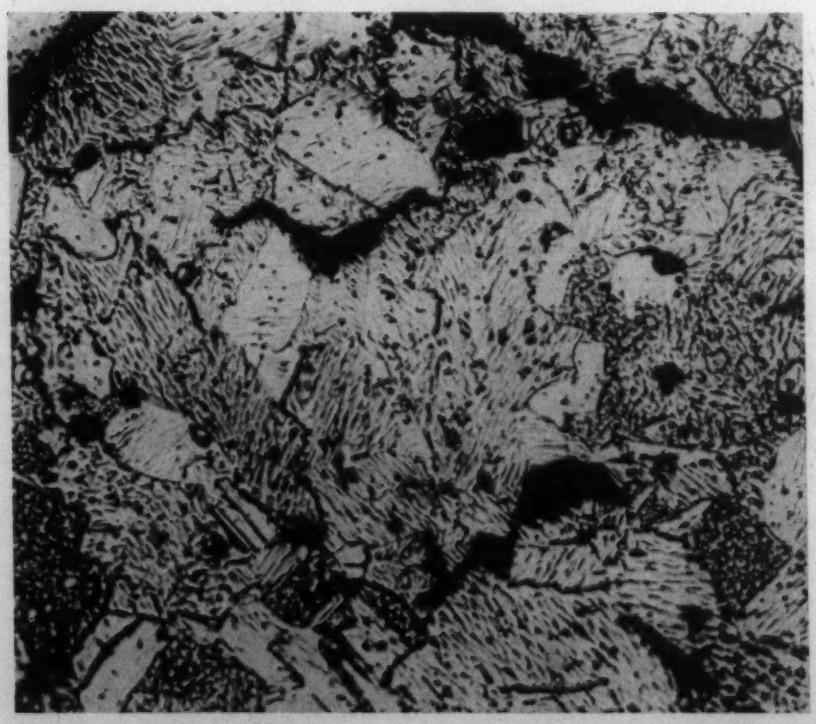


Fig. 5.—Microstructure of the 80:20 Alloy after Testing at 72 (Top), 1600 (Middle) and 1800 (Bottom) Deg. F. Etched with acidified ferric chloride solution. Magnifications 500 X.

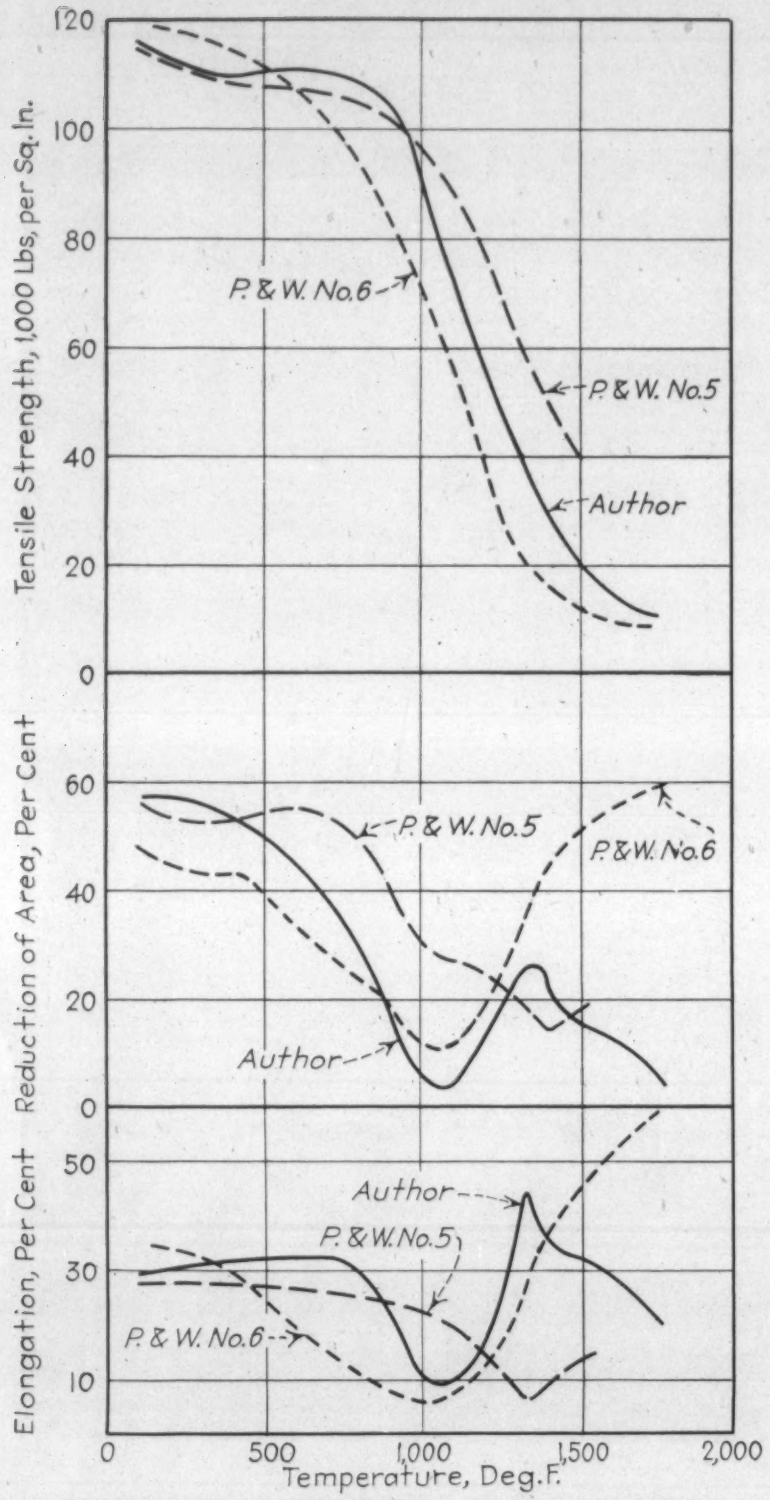


Fig. 6.—Comparison of Author's Results for Tophet A with those of Pilling and Worthington for other 80:20 Alloys. The compositions are given in Table I.

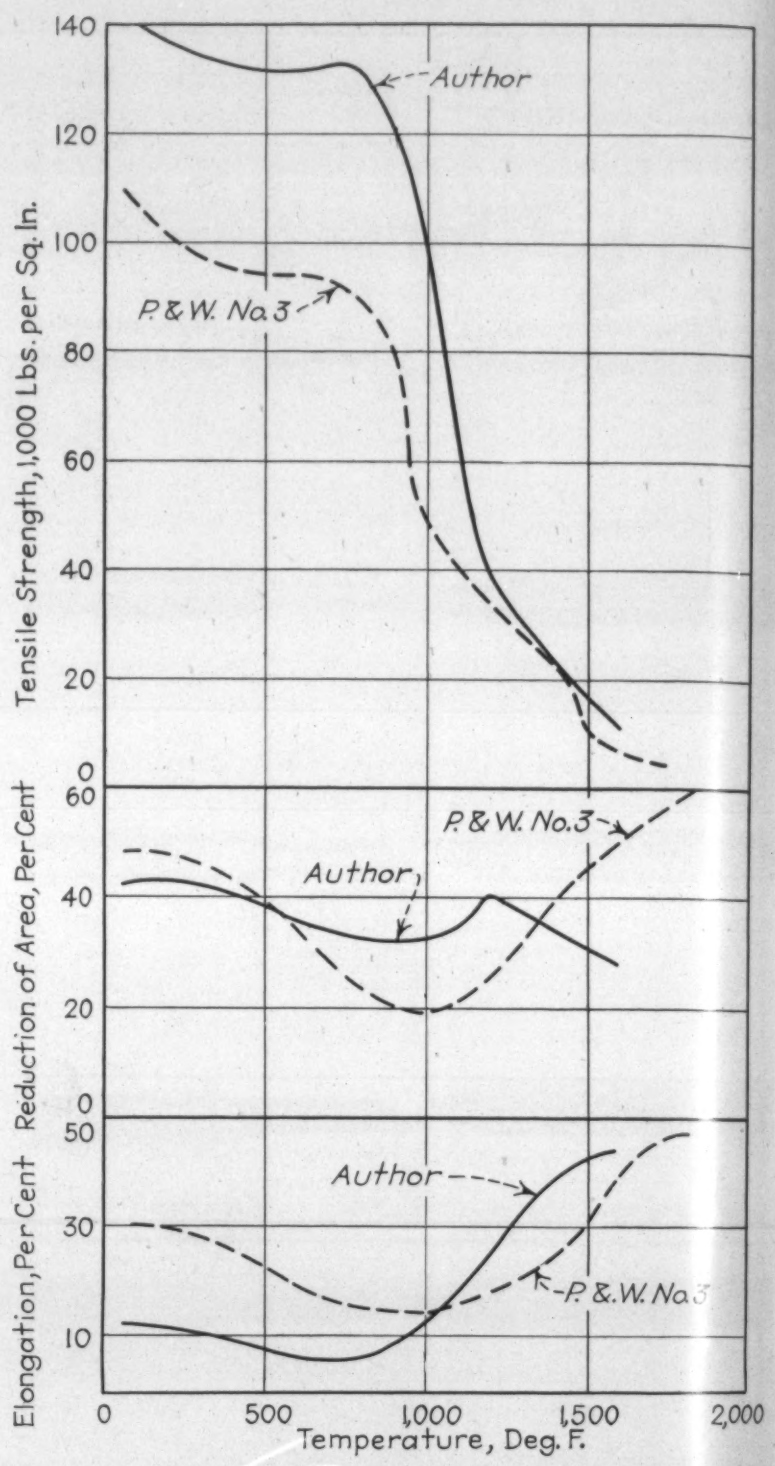


Fig. 7.—Comparison of Author's Results for Tophet C with those of Pilling and Worthington for Another 60:16 Alloy. The compositions are given in Table I.

1800 deg. F. the Tophet A was as strong as was the Tophet C at 1600 deg. F.

The deviation of the reduction of area curve of Tophet A from Pilling and Worthington's material No. 6, and that of Tophet C from their No. 3 at 1400-1600 deg. F. begins where inter-crystalline cracking was observed by the author. Alloys of these types are extremely sensitive to rate of loading, and different rates used by different experimenters may alter the results materially.

Acknowledgments

The author wishes to acknowledge gratefully the assistance offered by the following on this work: Dr. C. L. Mantell and J. F. Polak of the Wilbur B. Driver Co., for supplying the specimen material and photomicrographs respectively; Dr. S. S. Edmands, for permission to use the necessary laboratory facilities of Pratt Institute, Brooklyn; and Professor O. H. Henry, of the Polytechnic Institute of Brooklyn, for his valuable suggestions and counsel throughout the work.

The Hydride Process—II

by Peter P. Alexander

General Manager,
Metal Hydrides, Inc., Clifton, Mass.

Part I of this discussion was published in the September, 1937, issue of METALS AND ALLOYS, *pp. 263-264.*

ALL ELEMENTS OF THE FOURTH GROUP of the periodic table under suitable conditions form hydrides. The titanium sub-group is of particular interest since the elements of that sub-group form hydrides by direct action of hydrogen on these elements at a temperature above 300 deg. C. The present discussion, however, will be limited only to the first element of this sub-group, that is, titanium.

Preparation of Titanium

Titanium is the ninth most abundant element. According to F. W. Clarke,[1] titanium oxide constitutes 1 per cent of the earth's crust. A number of minerals contain titanium, yet only two, rutile (TiO_2) and ilmenite ($TiFeO_3$), are important sources of this element. Both rutile and ilmenite usually undergo chemical treatment before they are used for the production of metallic titanium. Purified titanium oxide is of special importance as a starting point in the production of titanium metal since this oxide is now available by the carload, of 99.5 per cent purity, and at a price of only 16¾c per lb.

Titanium was first isolated in 1825 by J. J. Berzelius,[2] who prepared metallic titanium by the reduction of potassium fluotitanate (K_2TiF_6) with sodium. Since that time a number of investigators have used several other methods in the preparation of titanium. These methods apart from small modifications could be classed in six groups:

1. The reduction of titanium tetrachloride ($TiCl_4$) with sodium.[3]
2. The reduction of titanium oxide (TiO_2) with metallic calcium.[4]
3. The reduction of titanium oxide with aluminum.[5]
4. The thermal dissociation of halogen compounds of titanium.[6]
5. The electro-deposition of titanium from fused salts.[7]
6. The reduction of titanium oxide with calcium hydride.[8]

All these methods have their merits as well as defects. The

Fig. 1. Producing a Cu-Ti Eutectic Alloy from Powdered Materials. At the left is a mixture of powdered copper and titanium hydride. In the center is a crucible into which the powdered mixture is placed. At the right is the ingot resulting from heating the crucible at 880 deg. C. It is a Cu-Ti eutectic alloy.

Fig. 2. Photomicrograph of the Cu-Ti Alloy (Ti-28%) × 200. Etched with $NH_4OH + H_2O_2$.

usual obstacle in the production of pure titanium on a commercial scale is either the high cost of production, or the contamination of titanium with the reducing agent.

The thermal dissociation of titanium chloride or iodide is of special interest since it gives ductile titanium. This method was first applied in 1908 by E. Defacqz and H. Copaux, and subsequently was developed to a high degree of perfection by A. E. Von Arkel and Dr. H. de Boer.[9] These last experimenters developed the technic of passing purified titanium iodide over incandescent tungsten filament on which titanium is deposited in concentric layers. After suitable heat treatment, the deposited titanium can be rolled into thin strips of metal.

Titanium produced by this method is quite ductile. It may be mentioned here that the same process was applied by Dr. de Boer for the production of ductile zirconium. This probably is the best process for the production of very pure titanium. Yet, at present, it is suitable only for use on a very small laboratory scale.

On the other hand, the hydride process, in which titanium oxide is reduced with calcium hydride, is probably one of the most suitable methods for the production of titanium on a large scale. Like other processes, the hydride process has its disadvantages as well as advantages. The disadvantage of this process is that titanium is always produced at first as a hydride, and only by subsequent degassing is it converted into metallic titanium. Even then the produced titanium contains an appreciable amount of hydrogen. In other words, titanium produced by the hydride process is never free from hydrogen. For several purposes this contamination is not desirable, and when hydrogen-free titanium is desired, titanium produced by other methods should be used.

This disadvantage in certain other fields, as will be shown below, has been turned into a very great advantage.

Titanium Hydride

As has been indicated, titanium, like all the metals of this sub-group, reacts directly with hydrogen. Yet the hydride which is formed, depends on the conditions under which the experiment was carried out. At present there is considerable difference of opinion with regard to the formula by which titanium hydride should be represented. This situation is due to the fact that different experimenters used different methods and so obtained titanium containing different amounts of hydrogen. It is quite likely that instead of one definite hydride, titanium forms several hydrides, depending on the method by which it is prepared.

A Klauber[14] produced gaseous titanium hydride which, when passed through a hot tube, was dissociated into hydrogen, and metallic titanium deposited on the walls of the tube. This hydride probably contains the largest amount of hydrogen. The other experimenters, instead of gaseous titanium hydrides, obtained solid hydrides.

M. Billy[10], by measuring the volume of hydrogen evolved by titanium hydride previously produced, suggested the formula, Ti_4H_5, for titanium hydride. It could be pointed out, however, that in this experiment, the degassed titanium probably still contained an appreciable amount of hydrogen. In fact, L. Weiss and H. Kaiser[11] stated that, once hydrogen is absorbed by titanium, it cannot be completely extracted even by long treatments in vacuum. They stated that even the vacuum-fused titanium, treated at 2000 deg. C., still contained 1.56 per cent of hydrogen.

It is now recognized that the amount of hydrogen absorbed by titanium depends not only on the temperature but also on the duration of the process of reduction of metal from oxide and even on the previous treatment of titanium oxide. It is also fairly well established that titanium, and other metals in this sub-group, take up more hydrogen at the moment of reduction of these metals from the oxide than they do when subsequently exposed to hydrogen. Mueller and Schwabe[12] for instance stated that, under such conditions, one volume of titanium absorbs 1800 volumes of hydrogen.

These various data, as well as those obtained by the writer, indicate that probably titanium forms several hydrides. However, by using the hydride process, the hydride most likely to be produced is that which could be represented by the formula, TiH_2. This hydride would lose part of its hydrogen if, during the production, it should be heated to too high a temperature, or after preparation it should be dried in a vacuum.

Properties of Titanium Hydride

Titanium hydride, when prepared by the reduction of titanium oxide with calcium hydride, comes in the state of very fine powder with every appearance of metallic titanium. It is not hygroscopic and is fairly resistant to the action of dilute hydrochloric acid. It can be exposed to atmospheric air at room temperature indefinitely without undergoing any changes. However, at high temperature, it gradually dissociates into hydrogen and the metal. The incipient dissociation in vacuum probably starts at about 100 deg. C. Yet up to 350 deg. C., it is very slow. Only

after the temperature is increased above 400 deg. C. does the dissociation become rapid. The complete dissociation is reached only at 1000 deg. C. Even then, as stated, a certain percentage of hydrogen is retained by the remaining metal.

The presence of hydrogen in titanium for certain purposes is very beneficial. It makes the handling of this material much safer than the handling of degassed metal. The powdered degassed metal, or titanium powder produced by methods giving hydrogen-free titanium, when heated above a certain temperature, ignites and burns almost instantaneously with great evolution of heat. And once ignited, the combustion of metallic titanium in powdered form cannot be extinguished by ordinary means.

The behavior of titanium hydride in this respect is quite different. For instance, if a small amount of titanium hydride is heated in a combustion boat over the flame of a Bunsen burner, no change will take place until the temperature of dissociation of the hydride is reached. When the powdered material is further heated above 350 deg. C., the hydrogen evolving from the powdered material will ignite and will burn with a quiet hydrogen flame, completely enveloping the powdered material. This will protect it from contact with air and rapid oxidation. This evolution of hydrogen will continue for a considerable time until most of the hydrogen is expelled and the temperature has reached 800 to 900 deg. C. Then the second reaction takes place and the degassed, or almost degassed titanium, ignites and burns in a fraction of a second with a great evolution of heat. The temperature of the burning titanium is that of dazzling white heat.

When the larger masses of titanium hydride, by some mistake, are overheated, as, for instance, during the drying process, they ignite very slowly with a hydrogen flame covering up the remaining charge. If the air is prevented from reaching the burning titanium hydride, the combustion of hydrogen, and therefore of the titanium hydride, will stop.

The transportation of titanium hydride is also much safer than that of metallic powdered titanium since there is no danger of spontaneous combustion of the powdered material.

Production of Copper-Titanium Alloys

The hydrogen present in large volumes in titanium cannot be considered as an impurity but rather as a valuable chemical reagent which is supplied in condensed form and which could be released at will either to supply 100 per cent pure hydrogen in activated form to produce certain chemical reactions, or to act as a flux to protect the expensive titanium from oxidation and nitrogenation when this material is used in metallurgical processes. One such application of hydrogen evolving from titanium hydride is found in the production of copper-titanium alloys.

The development of new non-ferrous alloys in the last decade has focused the attention of metallurgists on titanium as an alloying element. Hensel and Larsen[13] have shown that the binary copper alloy containing 2.58 per cent titanium has a yield point of 82,000 lbs. per sq. in., a tensile strength of 104,100 lbs. per sq. in., and an elongation of 20 per cent.

Other investigators have shown that the addition of titanium imparts to copper additional tensile strength

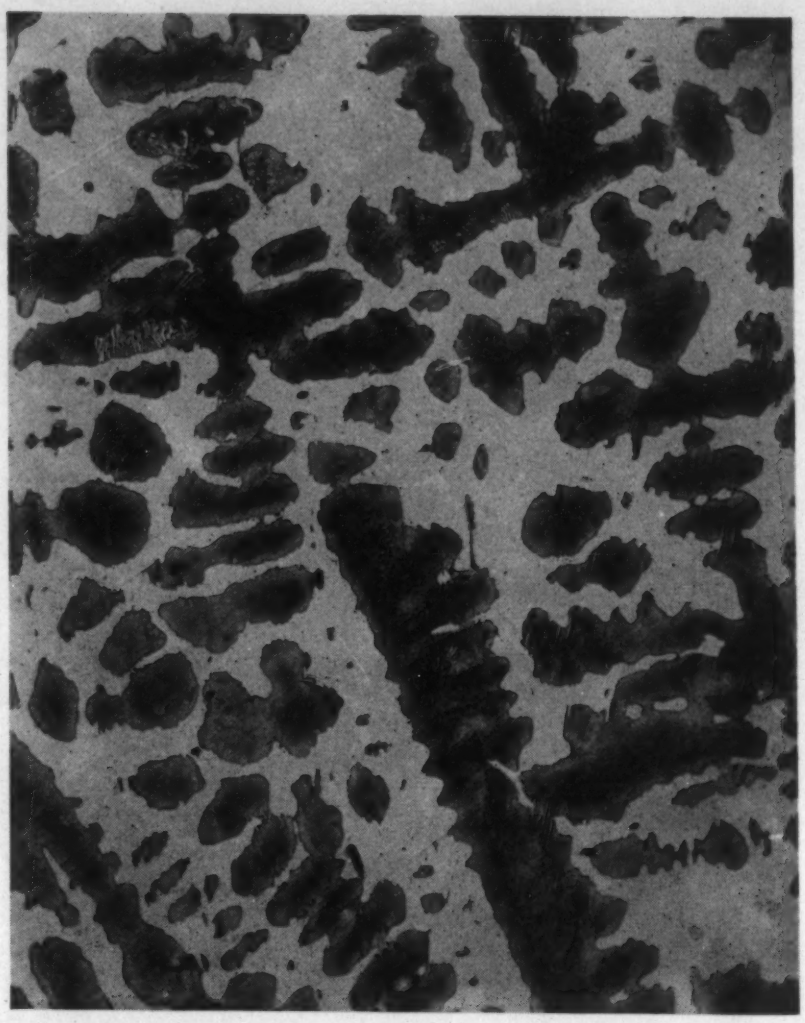


Fig. 3. Structure of a 15 per cent Ti-Cu Alloy Produced the Same as in Fig. 1, but at a Slightly Higher Temperature. X 100. Etched with $NH_4OH + H_2O_2$.

which is retained at high temperature to a greater degree than that of several other copper alloys. This indicates that copper-titanium alloys might find considerable use in such applications as condenser tubes, boilers, etc.

The production of titanium-copper is usually carried out by an addition of master alloy of copper and titanium. The usual composition of the master alloy is that of a eutectic of these two metals.

The production of titanium-copper eutectic alloy therefore has a definite purpose, and possibly would find in the future a considerable demand if such an alloy could be produced of sufficient purity and at comparatively low price.

The usual difficulty of introducing titanium into copper is due to their great difference in specific gravity and melting point as well as to the rapid oxidation and nitrogenation of titanium at high temperature. The specific gravity of copper is 8.94 and the melting point, 1083 deg. C.; whereas the specific gravity of titanium is 4.5 and the melting point, 1800 deg. C. In other words, if titanium is added to the molten bath of copper, it would rise immediately to the surface and would be subject to oxidation even in spite of the protective fluxes. Furthermore, molten copper contains a certain percentage of oxygen which of course would oxidize part of the introduced titanium.

Ti-Cu Alloy by a New Process

To eliminate these difficulties, a new process has been developed by Metal Hydrides, Inc., which takes advantage of the technic used in powder metallurgy and the special properties of titanium hydride. (Patents applied for in the

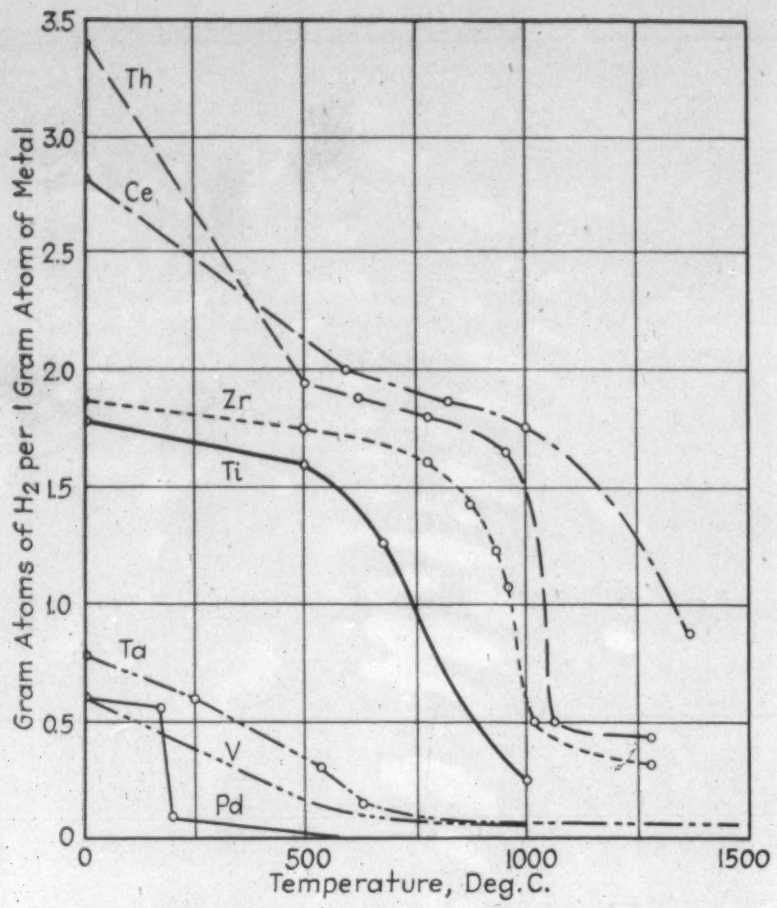


Fig. 4. Isobars for One Atmosphere of H_2 Showing the Number of Atoms of Hydrogen Absorbed by One Gram Atom of Different Metals at Various Temperatures.[15]

U. S., Canada and other countries.)

Since it is desired to produce a eutectic alloy, powdered titanium hydride and powdered copper, which now is available on the market in any quantity at a comparatively low price, are thoroughly mixed in the proportion of the eutectic composition; that is, titanium 28 per cent and copper 72 per cent. These are mixed in the ball mill until the distribution of titanium hydride particles is perfectly uniform throughout the mass of powdered copper. The powdered mixture is then simply poured into crucible A, shown on Fig. 1, and placed in a vacuum furnace.

As the temperature of the powdered mass is gradually rising, the titanium hydride begins to dissociate slowly. The evolving hydrogen reacts immediately with the thin layers of copper oxide always present on the grains of powdered copper, and the produced moisture with an excess of hydrogen is withdrawn from the powdered mass. Since at this stage, the evolution of hydrogen from titanium hydride is very rapid, each particle of that compound is surrounded by an atmosphere of nascent hydrogen which prevents the produced moisture from coming in contact with titanium and oxidizing it. By the time the temperature reaches 800 deg. C., all the particles of copper are absolutely free from any traces of oxide. They more or less weld together and the whole mass sinters and shrinks into a smaller volume. The particles of partly degassed titanium hydride therefore come in intimate contact with the clean surfaces of deoxidized copper.

As the temperature is rising still higher and reaches 878 deg. C., that is, the temperature of the melting point of copper-titanium eutectic, at the point of contact of copper and titanium particles there is a formation of liquid low-melting point alloy. Since copper and copper-rich alloys have a tendency to flow by capillarity in an atmosphere of hydrogen, over the clean surfaces of such metals as iron, titanium, etc., the formed droplet of liquid alloy does not remain in its initial position but spreads over the surface of the titanium particle. The pure titanium and pure copper again come in contact with the subsequent formation of another droplet of liquid low-melting point alloy. This continuous out-flow of the formed liquid alloy results in the gradual conversion of the total mass of titanium into titanium-copper eutectic alloy.

At the beginning of this process the whole powdered mass is solid and there is no tendency for titanium or titanium hydride to segregate. When the process is reaching the initial stage of formation of liquid droplets of eutectic alloy, the whole mass assumes a more or less pasty state and again the tendency of titanium to separate by gravity is checked. In the last stage of the process, when all of the titanium particles are converted into eutectic alloy, this phenomenon takes place simultaneously in all parts of the charge. The whole mass is now converted into a liquid alloy of uniform composition and specific gravity.

Since copper and copper-rich alloys do not dissolve hydrogen in solid state, the last traces of hydrogen escape from the alloy at the moment of solidification of the produced charge. The resulting ingots therefore come in the state of rather porous material which can be easily broken up with a hammer into small pieces or can even be crushed in a jaw-crusher. The dissociation of titanium hydride could be somewhat retarted by conducting operations, not in a vacuum, but in the atmosphere of hydrogen. This modification is used when a continuous operation of the furnace is desired.

The ingot in Fig. 1 shows that, in spite of the absence of any fluxes, its top surface is clean and absolutely free from any traces of oxidation. Fig. 2 shows the photomicrograph taken on the piece of alloy from the ingot shown in Fig. 1. Fig. 3 shows a photomicrograph of 15 per cent titanium-copper alloy produced by the same method but at slightly higher temperature.

This method of production of copper-titanium eutectic alloys utilizes the advantages of powder metallurgy to produce a fused alloy. In other words, the cast alloy is produced by putting together two solid metals and by heating them to a temperature way below the melting point of either of the metals.

It may also be pointed out that in this process of the production of alloys by mixing together two pure metals and using, as a flux, only hydrogen contained in one of the constituents, we eliminate the possibility of the contamination of the resulting alloy by the particles of flux, oxide, nitride, etc. The purity of alloys, therefore, will be determined only by the purity of the metals used in their production.

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AN EXTENDED ABSTRACT ON

LEAD-CALCIUM ALLOYS

FOR STORAGE BATTERIES

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Most of the information in this abstract appeared in a recent article[4] by U. B. Thomas, Jr., in Bell Laboratories Record; in addition, some data published in earlier papers[1, 2, 3] by Mr. Thomas and other Bell Laboratories investigators have been included to complete the picture. The specific source in any case is indicated in the text.

SEVEN YEARS AGO, experiments were conducted to determine the exact composition of the air in various telephone offices. Using the standard iodine-starch test, it was found that the "sulphur dioxide" concentration was distinctly greater near battery rooms during the period of overcharge. Specific tests showed that the gas was not sulphur dioxide, but it required a lengthy investigation to prove that the pseudo-sulphur dioxide was really stibine (antimony hydride).[1, 4]

As shown in Fig. 1, appreciable amounts of stibine are evolved only during the overcharge period when the nascent hydrogen is evolved at the negative antimony-lead plate, in which all antimony over about 0.25 per cent is present in the free state.[1, 4] The increase in stibine evolution after the battery has been idle is due to the extraction of antimony from the positive grid during charging, the deposition of this antimony on the sponge lead and the diffusion of the antimony to the surface of the negative grid.[1, 4]

The results of earlier tests in regard to the toxicity of stibine were confirmed, but the amounts involved in storage battery rooms are not sufficient to be dangerous.[1]

Need for An Alloy Superior to Pb-Sb

Since the leaching out and redeposition of antimony weakens the positive grid and forms local galvanic couples on the negative electrode that increase the rate of self discharge, it appeared desirable to attempt to develop a superior alloy. The alloying element should be electro-

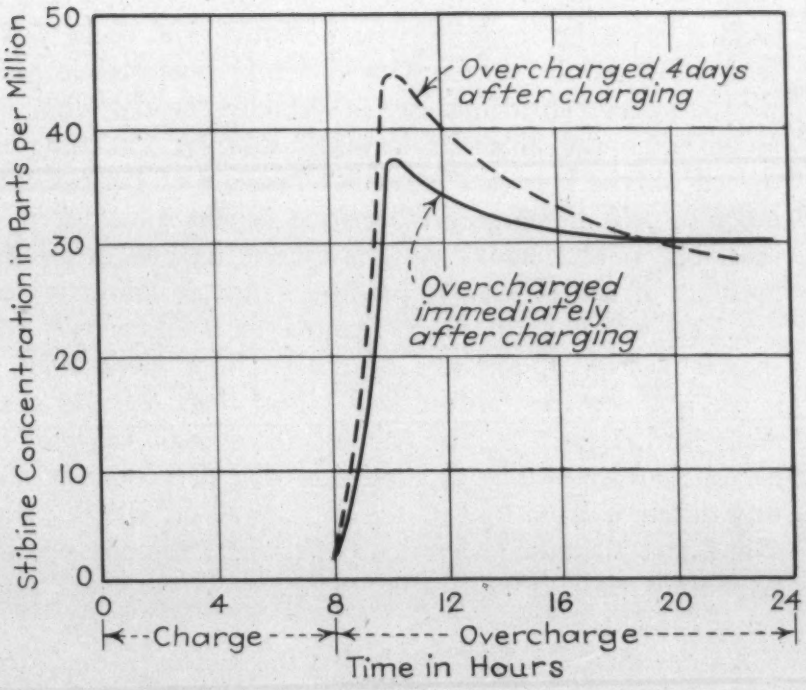

Fig. 1.—Stibine Concentration of Storage Battery Gases during Charge and Overcharge.

negative to lead, so that self discharge by local action would be impossible. Furthermore, it should have a low diffusivity at room temperature and should not be present as a net work, to avoid selective solution of the alloying element and consequent weakening of the plate. Other desirable properties would be a high electrical conductivity and low solidification shrinkage.[4]

Since calcium is electronegative to lead, the age-hardening calcium-lead alloys that had been developed for cable sheaths were considered.[3, 4] The age-hardening is due to the fact that about 0.1 per cent calcium is soluble in lead at the peritectic temperature (328.3 deg. C.) and only about 0.01 per cent at room temperature. Since the 0.1 per cent calcium-lead alloy consists of primary solid solu-

tion crystals with a submicroscopic dispersed phase (Pb_3Ca), whereas the 9 per cent antimony-lead alloy consists of dendritic crystals of the lead-rich phase surrounded by lead-antimony eutectic, the calcium-lead alloys would not be susceptible to weakening by leaching. An added advantage is the low diffusivity of calcium in lead at room temperatures.[3]

Mechanical Properties of Pb-Ca

Fig. 2 shows the tensile strength of various calcium-lead alloys after aging at room temperature for one week and holding at 100 deg. C. for 18 hrs.[3, 4] The maximum value of 8,000 lbs. per sq. in. for 0.1 per cent calcium is comparable to the strength of the 9 per cent antimony-lead alloy. There is no danger of softening at room temperature, since samples showed no decrease in tensile strength after eight years. The cold rolling of age-hardened calcium-lead alloys facilitates the precipitation of the compound (Pb_3Ca), but owing to its effect on the grain size, it does not always increase the tensile strength. For example, the tensile strength of 0.04 per cent calcium-lead was increased from 5,200 to 6,600 lbs. per sq. in. by cold rolling, whereas the strength of 0.08-0.10 per cent calcium-lead was slightly decreased.[3]

Electrochemical Properties of Pb-Ca

A simple qualitative test for sulphation or the loss of charge on an open circuit due to the slow corrosion of lead can be made by recording the potential-time curve for a lead alloy rod in sulphuric acid. The potential is practically constant until the lead is virtually covered with sulphate when the potential increases sharply. The time required for the potential break is a measure of the susceptibility to self discharge. Sulphation is very slow for pure lead, but is accelerated by atmospheric oxygen or by the presence of electronegative particles (such as antimony) on the lead which form short-circuited local elements.[2] As shown in Fig. 3, the loss of charge in a given time is much less for the calcium-lead alloys than for the antimony-lead alloys.[2, 4] The anodic and cathodic behavior of the calcium-lead alloys is similar to that of pure lead and very different from that of the antimony-lead alloys. Fig. 4 indicates that the deleterious effect of antimony on the sulphation time is noticeable even with very small antimony contents.[2, 4]

An unexpected advantage is that the hydrogen evolution during the overcharge period starts at a potential about 0.4 volt more positive for calcium-lead alloys and lead than for antimony-lead alloys. This means that less current is wasted in hydrogen evolution and more devoted to the purpose of changing the lead sulphate to lead when lead or calcium-lead plates are used.[2]

Other Advantages

The electrical conductivity of 0.1 per cent calcium-lead alloys is about 20 per cent higher than that of the 9 per cent antimony-lead. This is important in securing a uniform current distribution throughout the grid when large currents are drawn.[2, 4] The calcium-lead alloys have good casting properties (grids have been made with a thickness of only 0.07 in.), and can be welded, burned, drawn, extruded and stamped.[3, 4]

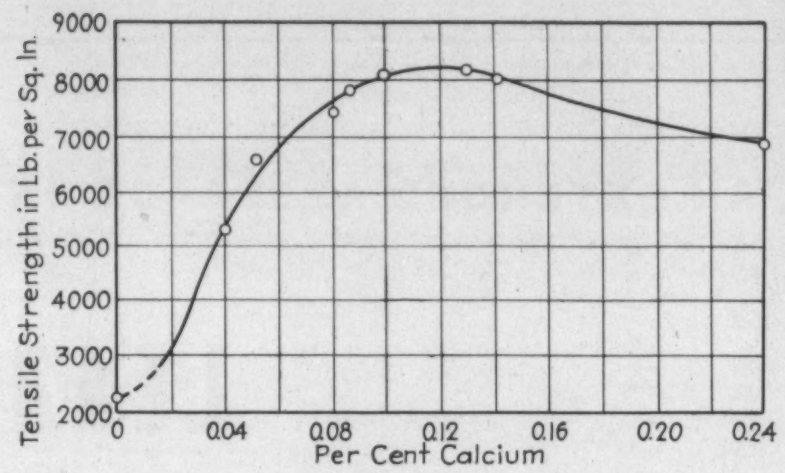

Fig. 2.—Variation of Tensile Strength with Calcium Content of Hardened Lead-Calcium Alloys.

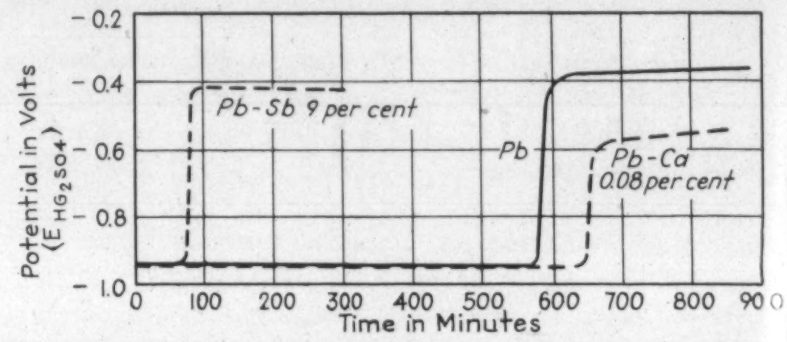

Fig. 3.—Typical Sulphation Curves for Lead, Lead-Antimony and Lead-Calcium in 7 N. H_2SO_4. Points were determined from the average of 5 tests carried out in an air thermostat at 25 ± 0.1 deg. C.

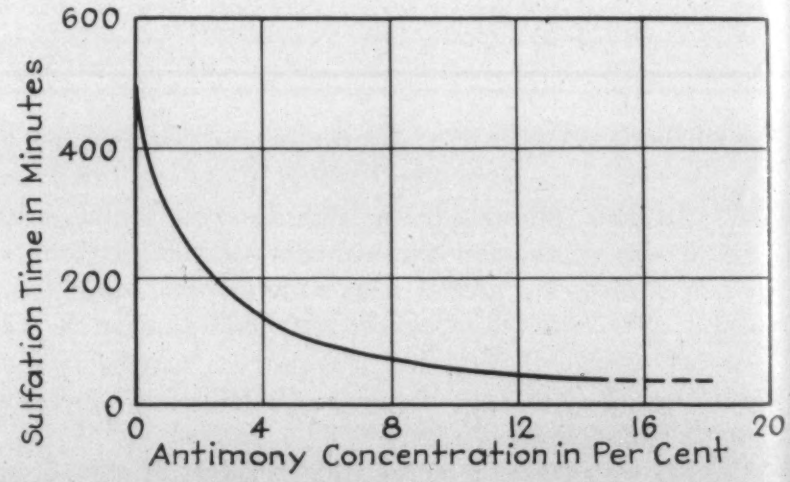

Fig. 4.—Effect of Antimony Concentration on the Sulphation Time of Lead-Antimony Alloys.

The raw materials are cheaper for the calcium-lead alloy than for the antimony-lead alloy, but the manufacturing costs may be greater. However, due to the increased life and cell efficiency, the 0.1 per cent calcium-lead alloy should be superior for storage battery grids and for Plante type plates.

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Corrosion of Some Alloys by Solutions

OF AMMONIUM SALTS IN LIQUID AMMONIA

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WHILE CORROSION PROBLEMS dealing with aqueous solutions have been the subject of extensive investigation, little effort has been made to extend such studies to non-aqueous systems. The Haber synthetic ammonia process has made available to the industry a solvent which can be produced in large quantity at a cost of about 3c per lb. Liquid ammonia has thus become one of the cheapest anhydrous solvents now available on the market. Its boiling point at atmospheric pressure is —33 deg. C, but reactions in which its use is involved are generally carried out at higher temperatures and in equipment designed especially for high pressure operation.

Liquid ammonia (NH_3) rivals water in its ability to take into solution inorganic compounds. It is far superior to water as a solvent for organic compounds. Interest in ammonia is furthermore enhanced by the fact that it may be looked upon as the parent substance of a whole class of nitrogen compounds[1] which are related to ammonia in much the same way as the ordinary acids and bases are to water. It is sufficient to state here that *ammonium salts act as acids when dissolved in liquid ammonia.* Since solutions of ammonium salts in liquid ammonia have already found use in a number of processes which have assumed technical significance it is obvious that the corrosive effect of such solutions is a factor of distinct importance to the industry.

A survey of the available information dealing with the action of ammonium salts in liquid ammonia upon metals[2] reveals the fact that such data is not only fragmentary, but very qualitative in nature. According to statements in the literature the metals beryllium, zinc, cadmium and magnesium dissolve in solutions of ammonium nitrate, ammonium chloride and ammonium iodide to form the corresponding nitrates, chlorides and iodides. Aluminum is said to be unaffected by Divers solution (a concentrated solution of ammonium nitrate in liquid ammonia), while gallium and thallium are attacked only to a limited extent. The rare earth metals are dissolved readily by ammonium salts in liquid ammonia. Lead and tin are said to be stable towards solutions of ammonium nitrate and ammonium bromide. Bismuth is not affected by Divers' solution.

Bergstrom[3] found that chromium and molybdenum are practically unaffected by ammonium nitrate solutions, but that manganese is readily attacked by ammonium nitrate, ammonium bromide and ammonium cyanide. Elements of the eighth group of the periodic system seem to be the most generally resistant to the action of solutions of ammonium salts in liquid ammonia. Iron is reported by Divers[4] to be unattacked by Divers' solution, whereas Davis, Olmstead and Lundstrom[5] report that both iron and steel are rapidly attacked by solutions of ammonium nitrate and ammonium thiocyanate. Bergstrom reports that iron is slowly attacked in the pure state, but more readily if several per cent of the oxide is present (rusty iron?). Bergstrom also found that nickel and cobalt are acted upon slowly by a solution of ammonium nitrate.

While information on the action of liquid ammonia solutions of ammonium salts upon metals is very incomplete, no data on the resistance of alloys has been made available to date. We are therefore presenting the results of a preliminary investigation which was carried out for the purpose of determining the resistance of some of the commoner alloy materials to liquid ammonia solutions of ammonium chloride, ammonium nitrate and ammonium thiocyanate.

Experimental

The corrosion tests were carried out at room temperature in sealed glass tubes (16 by 300 mm.) The alloy samples, averaging about five grams in weight, were first ground on a carborundum belt to give a uniform surface on all specimens, then weighed and placed in separate tubes. All tubes were calibrated to contain 15 cc. of solution and one gram of ammonium salt was used in each case to give solutions of comparable concentration. After the alloy specimen and ammonium salt had been placed in the tube the latter was cooled in a solid carbon dioxide-acetone bath and liquid ammonia added to give the proper volume

of solution. The tubes were immediately sealed to preclude entrance of moisture and then allowed to come to room temperature. The tubes were allowed to stand for three months and examined occasionally for evidences of chemical action. After this time period had elapsed the tubes were cooled again, opened and the solutions evaporated. The alloy specimens were cleaned, dried and weighed, and the loss in weight per square centimeter calculated.

The experimental results are presented in the Table 4. Where the loss in weight was found to be less than one milligram per square centimeter this fact is indicated by an asterisk (*). The compositions noted in the first column are those specified by the manufacturers or given in various handbooks.

Table of Corrosion of Some Alloys by Solutions of Ammonium Salts in Liquid Ammonia

Weight loss is given in grams per square centimeter.

Composition	Salt dissolved in liquid ammonia		
	NH_4Cl	NH_4NO_3	NH_4SCN
Alloys of Iron:			
10Fe, 20Cr, 68Ni	*	*	0.004
51Fe, 12Cr, 35Ni	*	*	0.003
58Fe, 20Cr, 20Ni	*	*	0.005
65Fe, 21Cr, 12Ni	*	*	0.003
68Fe, 8Cr, 22Ni	*	*	0.002
72Fe, 18Cr, 8Ni	*	*	0.003
68Fe, 30Cr	*	*	0.006
70Fe, 28Cr, 0.5Mn	*	*	0.001
73Fe, 25Cr	*	*	0.004
99Fe, 0.45Cu, 0.05Mo	0.003	0.029	0.002
99Fe, 1.C	0.004	0.003	0.004
99.8Fe	——	0.012	——
Alloys of Copper:			
99.8Cu, 1.1Cd	0.007	0.008	0.011
98.16Cu, 1.77Sn	0.006	0.005	0.005
96.1Cu, 1.86Sn, 2Al	0.005	0.003	0.005
95.5Cu, 4.2Sn, .14P	0.003	0.005	0.001
91Cu, 8Sn, .15P	0.002	0.007	0.001
90.1Cu, 7.3Sn, 2.3Zn	0.002	0.004	0.002
83.6Cu, 3.8Sn, 8.8Zn, 4.4Pb	0.005	0.004	0.003
81Cu, 4.1Sn, 8.14Zn, 6.5Pb	0.002	0.004	0.004
77.2Cu, 2.4Sn, 19.4Zn, 0.7Pb	0.003	0.001	0.002
76.1Cu, 18.1Zn, 4Ni, 1.64Si	0.005	0.003	0.003
64.36Cu, 5.34Zn, 29.71Ni	0.006	——	0.002
27Cu, 68Ni, 5Fe	0.035	——	0.001
Miscellaneous:			
100Ni	0.004	0.006	0.001
99.4Pb	0.118	0.013	0.001
94Pb, 6Sb	0.007	0.011	0.002

Discussion

In evaluating the results presented above, it is necessary to keep in mind that ammonium salts when dissolved in liquid ammonia produce solutions which are actually acidic in nature. Thus, a solution containing ammonium chloride may be regarded as analogous to a solution of hydrochloric acid in water. It should be pointed out, however, that the conditions are not exactly comparable—(1) because the action of such solutions upon metals is much more sluggish and (2) because the solubilities of the products in liquid ammonia are in many cases very different from the solubilities of these same substances in water.

The results of our tests indicate that chrome-nickel steels and high chromium steels are quite resistant to corrosion by solutions of both ammonium chloride and ammonium nitrate. It is quite evident that the addition of chromium to steel greatly increases the resistance to solutions of these "acids" in liquid ammonia, since various samples of iron and steel subjected to these same tests undergo appreciable attack.

These same iron alloys are readily attacked by solutions of ammonium thiocyanate. This finding is not altogether unexpected to those familiar with the solubilities of various compounds in non-aqueous solvents, since metallic thiocyanates are generally among the most easily soluble compounds. Unfortunately, the data do not give evidence of any correlation between composition and extent of corrosion.

The copper alloys listed in the table were readily attacked by all three solutions. This is very probably due to the fact that soluble cupric salts exist in liquid ammonia in the form of the very stable complexion, the tetramino-cupric ion, $Cu(NH_3)_4^{++}$. Solutions in contact with the various copper alloys invariably assumed the characteristic blue coloration, leading one to assume that corrosion involves at least partial solution of the copper in the cupric state.

The corrosion of chemical lead may serve to illustrate the difference between aqueous and liquid ammonia solutions of acids. At ordinary temperature dilute hydrochloric acid attacks lead slowly; corrosion by ammonium chloride in liquid ammonia is very marked. The addition of 6 per cent antimony (antimonial lead) increases materially resistance to the ammonium chloride solution.

Nickel, wrought iron and steel suffer appreciable corrosion by solutions of all three ammonium salts. Aluminum is not attacked by ammonium nitrate solution in liquid ammonia, which is presumably due to the fact that the oxide film on the metal is not dissolved or removed.

Our results must be considered directional in nature. They should serve to emphasize the need of more extended investigations of the phenomena of corrosion not only in liquid ammonia, but in other solvent systems where specific solutes impart especial chemical character to the resulting solutions.

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